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Quasi-equilibrium closure hierarchies for the Boltzmann equation

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Abstract

In this paper, explicit method of constructing approximations (the triangle entropy method) is developed for nonequilibrium problems. This method enables one to treat any complicated nonlinear functionals that fit best the physics of a problem (such as, for example, rates of processes) as new independent variables.

The work of the method is demonstrated on the Boltzmann's-type kinetics. New macroscopic variables are introduced (moments of the Boltzmann collision integral, or scattering rates). They are treated as independent variables rather than as infinite moment series. This approach gives the complete account of rates of scattering processes. Transport equations for scattering rates are obtained (the second hydrodynamic chain), similar to the usual moment chain (the first hydrodynamic chain). Various examples of the closure of the first, of the second, and of the mixed hydrodynamic chains are considered for the hard sphere model. It is shown, in particular, that the complete account of scattering processes leads to a renormalization of transport coefficients.

The method gives the explicit solution for the closure problem, provides thermodynamic properties of reduced models, and can be applied to any kinetic equation with a thermodynamic Lyapunov function.

Keywords: Entropy; MaxEnt; Kinetics; Boltzmann equation; Fokker–Planck equation; Model reduction

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0. Introduction

In this paper, explicit method of constructing approximations (the triangle entropy method (TEM) [1,2]) is developed for nonequilibrium problems of Boltzmann's-type kinetics, i.e., when the standard moments of distribution function become insufficient. This method enables one to treat any complicated nonlinear functionals that fit best the physics of a problem (such as, for example, rates of processes) as new independent variables.

The method is applied to the problem of derivation of hydrodynamics from the Boltzmann equation. New macroscopic variables are introduced (moments of the Boltzmann collision integral, or scattering rates). They are treated as independent variables rather than as infinite moment series. This approach gives the complete account of rates of scattering processes. Transport equations for scattering rates are obtained (the second hydrodynamic chain), similar to the usual moment chain (the first hydrodynamic chain).

Using the TEM, three different types of the macroscopic description are considered. The first type involves only moments of distribution functions, and results coincide with those of the Grad method in the Maximum Entropy version. The second type of description involves only scattering rates. Finally, the third type involves both the moments and the scattering rates (the mixed description).

The second and the mixed hydrodynamics are sensitive to the choice of the collision model. The second hydrodynamics is equivalent to the first hydrodynamics only for Maxwell molecules, and the mixed hydrodynamics exists for all other types of collision models.

Various examples of the closure of the first, of the second, and of the mixed hydrodynamic chains are considered for the hard sphere model. It is shown, in particular, that the complete account of scattering processes leads to a renormalization of transport coefficients.

The method gives the explicit solution for the closure problem, provides thermodynamic properties of reduced models, and can be applied to any kinetic equation with a thermodynamic Lyapunov function, for example, to the Fokker–Planck equation.

Reduction of description for dissipative kinetics assumes (explicitly or implicitly) the following picture (Fig. 1a): There exists a manifold of slow motions Ω_{slow} in the space of distributions. From the initial conditions the system goes quickly in a small neighborhood of the manifold, and after that moves slowly along it. The manifold of slow motion (slow manifold, for short) must be positively invariant: if a motion starts on the manifold at t_0, then it stays on the manifold at $t > t_0$. In some neighbourhood of the slow manifold the directions of fast motion could be defined. Of course, we mostly deal not with the invariant slow manifold, but with some approximate (ansatz) slow manifold Ω.

There are three basic problems in the model reduction:

(1) How to *construct* an approximate slow manifold;
(2) How to *project* the initial equation onto the constructed approximate slow manifold, i.e., how to split motions into fast and slow;

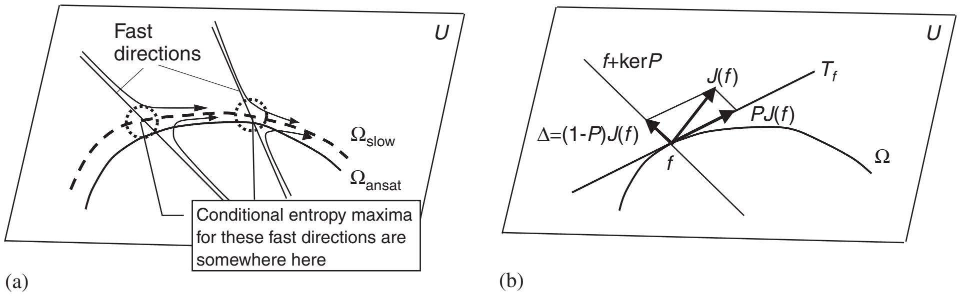

Fig. 1. (a) Fast–slow decomposition. Bold dashed line—slow invariant manifold; bold line—approximate invariant manifold; several trajectories and relevant directions of fast motion are presented schematically. (b) The geometrical structures of model reduction: U is the phase space, $J(f)$ is the vector field of the system under consideration: $\mathrm{d}f/\mathrm{d}t = J(f)$, Ω is an ansatz manifold, T_f is the tangent space to the manifold Ω at the point f, $PJ(f)$ is the projection of the vector $J(f)$ onto tangent space T_f, $\Delta = (1-P)J(f)$ is the defect of invariance, the affine subspace $f + \ker P$ is the plain of fast motions, and $\Delta \in \ker P$.

(3) How to *improve* the constructed manifold and the projector in order to make the manifold more invariant and the motion along it slower.

The first problem is often named "the closure problem", and its solution is the closure assumption; the second problem is "the projection problem". Sometimes these problems are discussed and solved simultaneously (for example, for the quasiequilibrium, or, which is the same, for MaxEnt closure assumptions [3–8]). Sometimes solution of the projection problem after construction of the ansatz is delayed. The known case of such a problem gives us the Tamm–Mott–Smith approximation in the theory of shock waves (see, for example Ref. [9]). However, if one has constructed the closure assumption which is at the same time the *invariant manifold* [9,11,12], then the projection problem disappears, because the vector field is always tangent to the invariant manifold. In this paper, we would like to add several new tools to the collection of methods for solving the closure problem. The second problem was discussed in Ref. [10]. We do not discuss here the third main problem of model reduction: How to improve the constructed manifold and the projector in order to make the manifold more invariant and the motion along it more slow. This discussion can be found in various works [9,11–14], and a broad review of the methods for invariant manifolds construction was presented in Refs. [15,16].

Our standard example in this paper is the Boltzmann equation, but most of the methods can be applied to an almost arbitrary kinetic equation with a convex thermodynamic Lyapunov function. Let us discuss the initial kinetic equation as an abstract ordinary differential equation[1]

$$\frac{\mathrm{d}f}{\mathrm{d}t} = J(f)\,, \tag{1}$$

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[1] Many of partial differential kinetic equations or integro-differential kinetic equations with suitable boundary conditions (or conditions at infinity) can be discussed as abstract ordinary differential equations in appropriate space of functions. The corresponding *semigroup* of shifts in time can be considered too.

where $f = f(q)$ is the distribution function, q is the point in the particle's phase space (for the Boltzmann equation), or in the configuration space (for the Fokker–Planck equation). This equation is defined in some domain U of a vector space of admissible distributions E.

The dissipation properties of system (1) are described by specifying the *entropy* S, the distinguished *Lyapunov function* which monotonically increases along solutions of Eq. (1). We assume that a concave functional S is defined in U, such that it takes maximum in an interior point $f^* \in U$. This point is termed the equilibrium.

For any dissipative system (1) under consideration in U, the derivative of S due to equation (1) must be nonnegative,

$$\left.\frac{\mathrm{d}S}{\mathrm{d}t}\right|_f = (D_f S)(J(f)) \geqslant 0\,, \tag{2}$$

where $D_f S$ is the linear functional, the differential of the entropy.

We always keep in mind the following picture (Fig. 1b). The vector field $J(f)$ generates the motion on the phase space U: $\mathrm{d}f/\mathrm{d}t = J(f)$. An ansatz manifold Ω is given, it is the current approximation to the invariant manifold.

The projected vector field $PJ(f)$ belongs to the tangent space T_f, and the equation $\mathrm{d}f/\mathrm{d}t = PJ(f)$ describes the motion along the ansatz manifold Ω (if the initial state belongs to Ω).

The choice of the projector P might be very important. There is a "duality" between the accuracy of slow invariant manifold approximation and restrictions on the projector choice. If Ω is an exactly invariant manifold, then the vector field $J(f)$ is tangent to Ω, and all projectors give the same result. If Ω gives a good smooth approximation for such an invariant manifold, then the set of admissible projectors is rather broad. On the other hand, there is the unique choice of the projector applicable for every (arbitrary) ansatz Ω [9,10], any other choice leads to violation of the Second Law in projected equations.

In the initial geometry of the fast–slow decomposition (Figs. 1a and b) the "slow variables" (or "macroscopic variables") are internal coordinates on the slow manifold, or on its approximation Ω. It is impossible, in general, to define these macroscopic variables as functionals of f outside these manifolds. Moreover, this definition cannot be unique.

The *moment parametrization* starts not from the manifold, but from the macroscopic variables defined in the whole U (Fig. 2a), and for the given variables it is necessary to find the corresponding slow manifold. Usually, these slow variables are linear functions (functionals), for example, hydrodynamic fields (density, momentum density, and pressure) are moments of one-particle distribution function $f(x, v)$. The moment vector M is the value of the linear operator m: $M = m(f)$. The moments values serve as internal coordinates on the (hypothetic) approximate slow

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(*footnote continued*)
Sometimes, when an essential theorem of existence and uniqueness of solution is not proven, it is possible to discuss a corresponding shift in time based on physical sense: the shift in time for physical system should exist. Benefits from the latter approach are obvious as well as its risk.

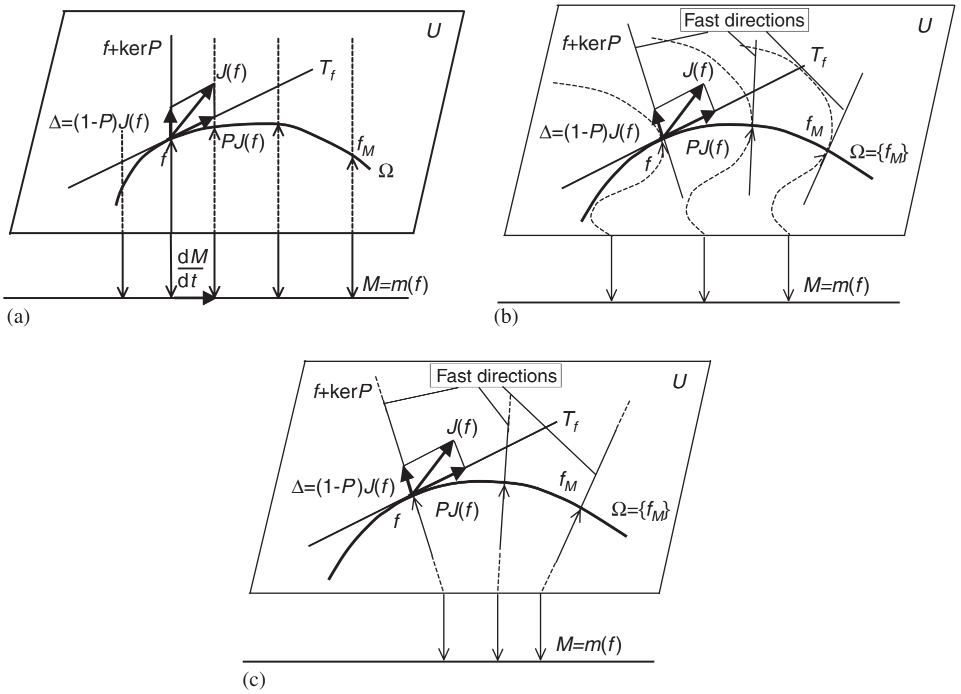

Fig. 2. Parametrization by macroscopic variables: linear (a), nonlinear (b) and layer-linear (c). Thin arrows illustrate the bijection $M \leftrightarrow f_M$. (a) Moment parametrization in fast–slow decomposition. Dashed lines—the plains of constant value of moments M. These plains coincide with directions of fast motion in the moment approximation. (b) Nonlinear macroscopic parametrization in fast–slow decomposition. Dashed curves—the surfaces of constant value of macroscopic variables M. Plains of fast motion are tangent to these surfaces. (c) Nonlinear, but layer-linear macroscopic parametrization in fast–slow decomposition. The surfaces of constant value of macroscopic variables M (dashed lines) are plain, but the dependence $m(f)$ is nonlinear. Plains of fast motion coincide with these plains.

manifold Ω. It means that points of Ω are parameterized by M, $\Omega = \{f_M\}$, and the *consistency condition* holds: $m(f_M) = M$. In the example with the one-particle distribution function f and the hydrodynamic fields $m(f)$ it means that slow manifold consists of distribution $f(x, v)$ parameterized by their hydrodynamic fields. For a given $\Omega = \{f_M\}$, the moment equation has a very simple form

$$\frac{\mathrm{d}M}{\mathrm{d}t} = m(J(f_M)) \tag{3}$$

and the corresponding equation for the projected motion on the manifold $\Omega = \{f_M\}$ is

$$\frac{\mathrm{d}f}{\mathrm{d}t} = (D_M f_M) m(J(f_M)) \,, \tag{4}$$

where $D_M f_M$ is the differential of the parametrization $M \mapsto f_M$.

How to find a manifold $\Omega = \{f_M\}$ for a given moment parametrization? A good initial approximation is the quasiequilibrium (or MaxEnt) approximations. The basic idea is: in the fast motion the entropy should increase, hence, the point of entropy maximum on the plane of rapid motion is not far from the slow manifold (Fig. 1a). If the moments M are really slow variables, and do not change significantly during the rapid motion, then the manifold of conditional entropy maxima f_M

$$S(f) \to \max, \quad m(f) = M \tag{5}$$

can serve as the appropriate ansatz for slow manifold.

Most of the works on nonequilibrium thermodynamics deal with quasiequilibrium approximations and corrections to them, or with applications of these approximations (with or without corrections). This viewpoint is not the only possible but it proves very efficient for the construction of a variety of useful models, approximations and equations, as well as methods to solve them. From time to time it is discussed in the literature, who was the first to introduce the quasiequilibrium approximations, and how to interpret them. At least a part of the discussion is due to a different role the quasiequilibrium plays in the entropy-conserving and the dissipative dynamics. The very first use of the entropy maximization dates back to the classical work of Gibbs [18], but it was first claimed for a principle of informational statistical thermodynamics by Jaynes [3]. Probably the first explicit and systematic use of quasiequilibria to derive dissipation from entropy-conserving systems was undertaken by Zubarev. Recent detailed exposition is given in Ref. [4]. For dissipative systems, the use of the quasiequilibrium to reduce description can be traced to the works of Grad on the Boltzmann equation [19]. A review of the informational statistical thermodynamics was presented in Ref. [20]. The connection between entropy maximization and (nonlinear) Onsager relations was also studied [21,22]. The viewpoint of the present authors was influenced by the papers by Rozonoer and co-workers, in particular, Refs. [5–7]. A detailed exposition of the quasiequilibrium approximation for Markov chains is given in the book [17] (Chapter 3, *Quasiequilibrium and entropy maximum*, pp. 92–122), and for the BBGKY hierarchy in the paper [8]. The maximum entropy principle was applied to the description the universal dependence the three-particle distribution function F_3 on the two-particle distribution function F_2 in classical systems with binary interactions [23]. For a discussion the quasiequilibrium moment closure hierarchies for the Boltzmann equation [6] see the papers [1,2,24]. A very general discussion of the maximum entropy principle with applications to dissipative kinetics is given in the review [25]. Recently the quasiequilibrium approximation with some further correction was applied to description of rheology of polymer solutions [26,27] and offerrofluids [28,29]. Quasiequilibrium approximations for quantum systems in the Wigner representation [30,31] was discussed very recently [32].

Formally, for quasiequilibrium approximation the linearity of the map $f \mapsto m(f)$ is not necessary, and the optimization problem (5) could be studied for nonlinear conditions $m(f) = M$ (Fig. 2b). Nevertheless, problem (5) with nonlinear conditions loose many important properties caused by concavity of S. The technical compromise is the problem with a nonlinear map m, but linear restrictions

$m(f) = M$. It is possible when preimages of points for the map m are plain (Fig. 2c). Such a "layer-linear" approximation for a generic smooth map $m_0 : f \mapsto M$ could be created as follows. Let Ω_0 be a smooth submanifold in U. In some vicinity of Ω_0 we define a map m

$$m(f) = m_0(f_0) \quad \text{if} \quad (Dm_0)_{f_0}(f - f_0) = 0\,, \tag{6}$$

where f_0 are points from Ω_0 and $(Dm_0)_{f_0}$ is the differential of m_0 at the point f_0. This definition means that $m(f) = m_0(f_0)$ if $m_0(f)$ coincides with $m_0(f_0)$ in the linear approximation. Eq. (6) defines a smooth layer-linear map m in a vicinity of Ω_0 under some general transversality condition. The layer-linear parametrization was introduced in Ref. [34] for the construction of generalized model equations for the Boltzmann kinetics.

Let us take Ω_0 as an initial approximation for the slow manifold. Two basic ways for its improvement are: (i) manifold correction and (ii) manifold extension. On the first way we should find a shifted manifold that is better approximate slow invariant manifold. The list of macroscopic variables remains the same. On the second way we extend the list of macroscopic variables, and, hence, extend the manifold Ω_0. The Chapman–Enskog method [33] gives the example of manifold correction in the form of Taylor series expansion, the direct Newton method gives better results [9,11,15,16,38,44]. The second way (the extension) is the essence of EIT—extended irreversible thermodynamics [43]. This paper is focused on the manifold extensions also.

Usually moments are graduated in a natural order, by degree of polynomials: concentration (zero order of velocity), average momentum density (first-order), kinetic energy (second-order), stress tensor (second-order), heat flux (third-order), etc. The normal logic of EIT is the extension of the list of variables by addition of the next-orders irreducible moment tensors. But there is another logic. In general, for the set of moments M that parametrizes Ω_0 a time derivative is a known function of f: $\mathrm{d}M/\mathrm{d}t = F_M(f)$. We propose to construct new macroscopic variables from $F_M(f)$. It allows to achieve the best possible approximation for $\mathrm{d}M/\mathrm{d}t$ through extended variables. For this nonlinear variables we use the layer-linear approximation (6), as well as a layer-quadratic approximation for the entropy. This (layer) linearization of the problem near current approximation follows lessons of the Newton method—linearization of an equation in the point of current approximation or nearby.

It should be stressed that "layer-linear" does not mean "linear", and the modified choice of new variables implies no additional restrictions, but it is a more direct way to dynamic invariance. Below this approach is demonstrated on the Boltzmann equation.

1. Difficulties of classical methods of the Boltzmann equation theory

The Boltzmann equation remains the most inspiring source for the model reduction problems. The first systematic and (at least partially) successful method of constructing invariant manifolds for dissipative systems was the celebrated *Chapman–Enskog method* [33] for the Boltzmann kinetic equation. The main difficulty of the Chapman–Enskog method [33] are "nonphysical" properties of high-order approximations. This was stated by a number of authors and was discussed in detail in Ref. [35]. In particular, as it was noted in Ref. [36], the Burnett approximation results in a short-wave instability of the acoustic spectra. This fact contradicts the *H*-theorem (cf. in Ref. [36]). The Hilbert expansion contains secular terms [35]. The latter contradicts the *H*-theorem.

The other difficulties of both of these methods are: the restriction upon the choice of the initial approximation (the local equilibrium approximation), the requirement for a small parameter, and the usage of slowly converging Taylor expansion. These difficulties never allow a direct transfer of these methods on essentially none-quilibrium situations.

The main difficulty of the Grad method [19] is the uncontrollability of the chosen approximation. An extension of the list of moments can result in a certain success, but it can also give nothing. Difficulties of moment expansion in the problems of shock waves and sound propagation are discussed in Ref. [35].

Many attempts were made to refine these methods. For the Chapman–Enskog and Hilbert methods these attempts are based in general on some better rearrangement of expansions (e.g., neglecting high-order derivatives [35], reexpanding [35], Pade approximations and partial summing [1,37,39,40], etc.). This type of work with formal series is widespread in physics. Sometimes the results are surprisingly good—from the renormalization theory in quantum fields to the Percus–Yevick equation and the ring-operator in statistical mechanics. However, one should realize that success cannot be guaranteed.

Attempts to improve the Grad method are based on quasiequilibrium approximations [5,6]. It was found in Ref. [6] that the Grad distributions are linearized versions of appropriate quasiequilibrium approximations (see also Refs. [1,2,24]). A method which treats fluxes (e.g., moments with respect to collision integrals) as independent variables in a quasiequilibrium description was introduced in Refs. [1,2,41,42], and will be discussed later.

The important feature of quasiequilibrium approximations is that they are always thermodynamic, i.e., they are consistent with the *H*-theorem by construction.

2. Triangle entropy method

In the present subsection, which is of introductory character, we shall refer, to be specific, to the Boltzmann kinetic equation for a one-component gas whose state (in the microscopic sense) is described by the one-particle distribution function $f(\boldsymbol{v},\boldsymbol{x},t)$ depending on the velocity vector $\boldsymbol{v}=\{v_k\}_{k=1}^3$, the spatial position $\boldsymbol{x}=\{x_k\}_{k=1}^3$ and time t. The Boltzmann equation describes the evolution of f and in the absence of external forces is

$$\partial_t f + v_k \partial_k f = Q(f,f)\,, \tag{7}$$

where $\partial_t \equiv \partial/\partial t$ is the time partial derivative, $\partial_k \equiv \partial/\partial x_k$ is the partial derivative with respect to kth component of $\boldsymbol{x}$, summation in two repeating indices is assumed, and $Q(f,f)$ is the collision integral (its concrete form is of no importance right now, just note that it is functional-integral operator quadratic with respect to f).

The Boltzmann equation possesses two properties principal for the subsequent reasoning:

(1) There exist five functions $\psi_\alpha(\boldsymbol{v})$ (additive collision invariants), $1, \boldsymbol{v}, v^2$ such that for any their linear combination with coefficients depending on $\boldsymbol{x}, t$ and for arbitrary f the following equality is true:

$$\int \sum_{\alpha=1}^{5} a_\alpha(\boldsymbol{x}, t)\psi_\alpha(\boldsymbol{v})Q(f,f)\,\mathrm{d}\boldsymbol{v} = 0\,, \tag{8}$$

provided the integrals exist.

(2) Eq. (7) possesses global Lyapunov functional: the H-function,

$$H(t) \equiv H[f] = \int f(\boldsymbol{v}, \boldsymbol{x}, t)\,\ln f(\boldsymbol{v}, \boldsymbol{x}, t)\,\mathrm{d}\boldsymbol{v}\,\mathrm{d}\boldsymbol{x}\,, \tag{9}$$

the derivative of which by virtue of Eq. (7) is nonpositive under appropriate boundary conditions:

$$\mathrm{d}H(t)/\mathrm{d}t \leqslant 0\,. \tag{10}$$

Grad's method [19] and its variants construct closed systems of equations for macroscopic variables when the latter are represented by moments (or, more general, linear functionals) of the distribution function f (hence their alternative name is the "moment methods"). The maximum entropy method for the Boltzmann equation consists in the following. A finite set of moments describing the macroscopic state is chosen. The distribution function of the quasiequilibrium state under given values of the chosen moments is determined, i.e., the problem is solved

$$H[f] \to \min \quad \text{for } \hat{M}_i[f] = M_i,\ i = 1, \ldots, k\,, \tag{11}$$

where $\hat{M}_i[f]$ are linear functionals with respect to f; M_i are the corresponding values of chosen set of k macroscopic variables. The quasiequilibrium distribution function $f^*(\boldsymbol{v}, M(\boldsymbol{x}, t))$, $M = \{M_1, \ldots, M_k\}$, parametrically depends on M_i, its dependence on space $\boldsymbol{x}$ and on time t being represented only by $M(\boldsymbol{x}, t)$. Then the obtained f^* is substituted into the Boltzmann equation (7), and operators $\hat{M}_i$ are applied on the latter formal expression.

In the result we have closed systems of equations with respect to $M_i(\boldsymbol{x}, t)$, $i = 1, \ldots, k$:

$$\partial_t M_i + \hat{M}_i[\boldsymbol{v}_k \partial_k f^*(\boldsymbol{v}, M)] = \hat{M}_i[Q(f^*(\boldsymbol{v}, M), f^*(\boldsymbol{v}, M))]\,. \tag{12}$$

The following heuristic explanation can be given to the entropy method. A state of the gas can be described by a finite set of moments on some time scale θ only if all the other moments ("fast") relax on a shorter time scale time $\tau, \tau \ll \theta$, to their values determined by the chosen set of "slow" moments, while the slow ones almost do not change appreciably on the time scale τ. In the process of the fast relaxation the

H-function decreases, and in the end of this fast relaxation process a quasiequilibrium state sets in with the distribution function being the solution of problem (11). Then "slow" moments relax to the equilibrium state by virtue of (12).

The entropy method has a number of advantages in comparison with the classical Grad's method. First, being not necessarily restricted to any specific system of orthogonal polynomials, and leading to solving an optimization problem, it is more convenient from the technical point of view. Second, and ever more important, the resulting quasiequilibrium H-function, $H^*(M) = H[f^*(\boldsymbol{v}, M)]$, decreases due of the moment equations (12).

It is easy to find examples when the interesting macroscopic parameters are nonlinear functionals of the distribution function. In the case of the one-component gas these are the integrals of velocity polynomials with respect to the collision integral $Q(f,f)$ of (7) (scattering rates of moments). For chemically reacting mixtures these are the reaction rates, and so on. If the characteristic relaxation time of such nonlinear macroscopic parameters is comparable with that of the "slow" moments, then they should be also included into the list of "slow" variables on the same footing.

In this paper we develop the *TEM* for constructing closed systems of equations for nonlinear (in a general case) macroscopic variables. Let us outline the scheme of this method.

Let a set of macroscopic variables be chosen: linear functionals $\hat{M}[f]$ and nonlinear functionals (in a general case) $\hat{N}[f] : \hat{M}[f] = \{\hat{M}_1[f], \dots, \hat{M}_k[f]\}$, $\hat{N}[f] = \{\hat{N}_1[f], \dots, \hat{N}_l[f]\}$. Then, just as for problem (11), the first quasiequilibrium approximation is constructed under fixed values of the linear macroscopic parameters M

$$H[f] \to \min \quad \text{for } \hat{M}_i[f] = M_i, \ i = 1, \dots, k \tag{13}$$

and the resulting distribution function is $f^*(\boldsymbol{v}, M)$. After that, we seek the true quasiequilibrium distribution function in the form

$$f = f^*(1 + \varphi)\,, \tag{14}$$

where φ is a deviation from the first quasiequilibrium approximation. In order to determine φ, the second quasiequilibrium approximation is constructed. Let us denote $\Delta H[f^*, \varphi]$ as the quadratic term in the expansion of the H-function into powers of φ in the neighbourhood of the first quasiequilibrium state f^*. The distribution function of the second quasiequilibrium approximation is the solution to the problem,

$$\begin{aligned} &\Delta H[f^*, \varphi] \to \min \quad \text{for} \\ &\hat{M}_i[f^*\varphi] = 0, \ i = 1, \dots, k, \quad \Delta\hat{N}_j[f^*, \varphi] = \Delta N_j, \ j = 1, \dots, l\,, \end{aligned} \tag{15}$$

where $\Delta\hat{N}_j$ are linear operators characterizing the linear with respect to φ deviation of (nonlinear) macroscopic parameters N_j from their values, $N_j^* = \hat{N}_j[f^*]$, in the first quasiequilibrium state. Note the importance of the homogeneous constraints $\hat{M}_i[f^*\varphi] = 0$ in problem (15). Physically, it means that the variables ΔN_j are "slow" in the same sense, as the variables M_i, at least in the small neighbourhood of the first quasiequilibrium f^*. The obtained distribution function

$$f = f^*(\boldsymbol{v}, M)(1 + \varphi^{**}(\boldsymbol{v}, M, \Delta N)) \tag{16}$$

is used to construct the closed system of equations forr the macroparameters M, and ΔN. Because the functional in problem (15) is quadratic, and all constraints in this problem are linear, it is always explicitly solvable.

Further in this section some examples of using the TEM for the one-component gas are considered. Applications to chemically reacting mixtures were discussed in Ref. [41].

3. Linear macroscopic variables

Let us consider the simplest example of using the TEM, when all the macroscopic variables of the first and of the second quasiequilibrium states are the moments of the distribution function.

3.1. Quasiequilibrium projector

Let $\mu_1(\boldsymbol{v}), \dots, \mu_k(\boldsymbol{v})$ be the microscopic densities of the moments $M_1(\boldsymbol{x}, t), \dots, M_k(\boldsymbol{x}, t)$ which determine the first quasiequilibrium state

$$M_i(\boldsymbol{x}, t) = \int \mu_i(\boldsymbol{v}) f(\boldsymbol{v}, \boldsymbol{x}, t) \, \mathrm{d}\boldsymbol{v} \tag{17}$$

and let $\nu_1(\boldsymbol{v}), \dots, \nu_l(\boldsymbol{v})$ be the microscopic densities of the moments $N_1(\boldsymbol{x}, t), \dots, N_l(\boldsymbol{x}, t)$ determining together with (7) the second quasiequilibrium state

$$N_i(\boldsymbol{x}, t) = \int \nu_i(\boldsymbol{v}) f(\boldsymbol{v}, \boldsymbol{x}, t) \, \mathrm{d}\boldsymbol{v} \, . \tag{18}$$

The choice of the set of the moments of the first and second quasiequilibrium approximations depends on a specific problem. Further on we assume that the microscopic density $\mu \equiv 1$ corresponding to the normalization condition is always included in the list of microscopic densities of the moments of the first quasiequilibrium state. The distribution function of the first quasiequilibrium state results from solving the optimization problem

$$H[f] = \int f(\boldsymbol{v}) \ln f(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} \to \min \tag{19}$$

for $\int \mu_i(\boldsymbol{v}) f(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = M_i, \ i = 1, \dots, k$.

Let us denote by $M = \{M_1, \dots, M_k\}$ the moments of the first quasiequilibrium state, and by $f^*(\boldsymbol{v}, M)$ let us denote the solution of problem (19).

The distribution function of the second quasiequilibrium state is sought in the form

$$f = f^*(\boldsymbol{v}, M)(1 + \varphi) \, . \tag{20}$$

Expanding the H-function (9) in the neighbourhood of $f^*(\boldsymbol{v}, M)$ into powers of φ to second-order we obtain

$$\Delta H(\boldsymbol{x}, t) \equiv \Delta H[f^*, \varphi] = H^*(M) + \int f^*(\boldsymbol{v}, M) \ln f^*(\boldsymbol{v}, M)\varphi(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} + \frac{1}{2}\int f^*(\boldsymbol{v}, M)\varphi^2(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v}\,, \tag{21}$$

where $H^*(M) = H[f^*(\boldsymbol{v}, M)]$ is the value of the H-function in the first quasiequilibrium state.

When searching for the second quasiequilibrium state, it is necessary that the true values of the moments M coincide with their values in the first quasiequilibrium state, i.e.,

$$M_i = \int \mu_i(\boldsymbol{v}) f^*(\boldsymbol{v}, M)(1 + \varphi(\boldsymbol{v}))\,\mathrm{d}\boldsymbol{v} = \int \mu_i(\boldsymbol{v}) f^*(\boldsymbol{v}, M)\,\mathrm{d}\boldsymbol{v} = M_i^*, \quad i = 1, \ldots, k\,. \tag{22}$$

In other words, the set of the homogeneous conditions on φ in the problem (15)

$$\int \mu_i(\boldsymbol{v})\, f^*(\boldsymbol{v}, M)\varphi(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} = 0, \quad i = 1, \ldots, k \tag{23}$$

ensures a shift (change) of the first quasiequilibrium state only due to the new moments $N_1, \ldots, N_l$. In order to take this condition into account automatically, let us introduce the following inner product structure:

(1) Define the scalar product

$$(\psi_1, \psi_2) = \int f^*(\boldsymbol{v}, M)\psi_1(\boldsymbol{v})\psi_2(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v}\,. \tag{24}$$

(2) Let E_μ be the linear hull of the set of moment densities $\{\mu_1(\boldsymbol{v}), \ldots, \mu_k(\boldsymbol{v})\}$. Let us construct a basis of E_μ $\{e_1(\boldsymbol{v}), \ldots, e_r(\boldsymbol{v})\}$ that is orthonormal in the sense of the scalar product (24):

$$(e_i, e_j) = \delta_{ij} \tag{25}$$

i, $j = 1, \ldots, r$; δ_{ij} is the Kronecker delta.

(3) Define a projector $\hat{P}^*$ on the first quasiequilibrium state

$$\hat{P}^*\psi = \sum_{i=1}^{r} e_i(e_i, \psi)\,. \tag{26}$$

The projector $\hat{P}^*$ is orthogonal: for any pair of functions ψ_1, ψ_2,

$$(\hat{P}^*\psi_1, (\hat{1} - \hat{P}^*)\psi_2) = 0\,, \tag{27}$$

where $\hat{1}$ is the unit operator. Then condition (23) amounts to

$$\hat{P}^* \varphi = 0 \tag{28}$$

and the expression for the quadratic part of the H-function (21) takes the form

$$\Delta H[f^*, \varphi] = H^*(M) + (\ln f^*, \varphi) + (1/2)(\varphi, \varphi) \, . \tag{29}$$

Now, let us note that the function $\ln f^*$ is invariant with respect to the action of the projector $\hat{P}^*$:

$$\hat{P}^* \ln f^* = \ln f^* \, . \tag{30}$$

This follows directly from the solution of problem (19) using of the method of Lagrange multipliers:

$$f^* = \exp \sum_{i=1}^{k} \lambda_i(M) \mu_i(\boldsymbol{v}) \, ,$$

where $\lambda_i(M)$ are Lagrange multipliers. Thus, if condition (28) is satisfied, then from (27) and (30) it follows that

$$(\ln f^*, \varphi) = (\hat{P}^* \ln f^*, (\hat{1} - \hat{P}^*)\varphi) = 0 \, .$$

Condition (28) is satisfied automatically, if ΔN_i are taken as follows:

$$\Delta N_i = ((\hat{1} - \hat{P}^*)\nu_i, \varphi), \quad i = 1, \dots, l \, . \tag{31}$$

Thus, problem (15) of finding the second quasiequilibrium state reduces to

$$\Delta H[f^*, \varphi] - H^*(M) = (1/2)(\varphi, \varphi) \to \min$$
$$\text{for } ((\hat{1} - \hat{P}^*)\nu_i, \varphi) = \Delta N_i, \ i = 1, \dots, l \, . \tag{32}$$

In the remainder of this section we demonstrate how the TEM is related to Grad's moment method.

3.2. Ten-moment Grad approximation

Let us take the five additive collision invariants as moment densities of the first quasiequilibrium state:

$$\mu_0 = 1, \quad \mu_k = v_k \, (k = 1, 2, 3), \quad \mu_4 = \frac{mv^2}{2} \, , \tag{33}$$

where v_k are Cartesian components of the velocity, and m is particle's mass. Then the solution to problem (19) is the local Maxwell distribution function $f^{(0)}(\boldsymbol{v}, \boldsymbol{x}, t)$:

$$f^{(0)} = n(\boldsymbol{x}, t) \left(\frac{2\pi k_{\mathrm{B}} T(\boldsymbol{x}, t)}{m} \right)^{-3/2} \exp\left\{ - \frac{m(\boldsymbol{v} - \boldsymbol{u}(\boldsymbol{x}, t))^2}{2 k_{\mathrm{B}} T(\boldsymbol{x}, t)} \right\} , \tag{34}$$

where

$$n(\boldsymbol{x},t)=\int f(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v}\,\text{is local number density,}$$
$$\boldsymbol{u}(\boldsymbol{x},t)=n^{-1}(\boldsymbol{x},t)\int f(\boldsymbol{v})\boldsymbol{v}\,\mathrm{d}\boldsymbol{v}\,\text{is the local flow density,}$$
$$T(\boldsymbol{x},t)=\frac{m}{3k_{\mathrm{B}}}n^{-1}(\boldsymbol{x},t)\int f(\boldsymbol{v})(\boldsymbol{v}-\boldsymbol{u}(\boldsymbol{x},t))^2\,\mathrm{d}\boldsymbol{v}\,\text{is the local temperature,}$$
$$k_{\mathrm{B}}\,\text{is the Boltzmann constant.}$$

Orthonormalization of the set of moment densities (33) with the weight (34) gives one of the possible orthonormal basis

$$e_0=\frac{5k_{\mathrm{B}}T-m(\boldsymbol{v}-\boldsymbol{u})^2}{(10n)^{1/2}k_{\mathrm{B}}T},$$
$$e_k=\frac{m^{1/2}(v_k-u_k)}{(nk_{\mathrm{B}}T)^{1/2}}\quad(k=1,2,3)\,,$$
$$e_4=\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{(15n)^{1/2}k_{\mathrm{B}}T}\,. \tag{35}$$

For the moment densities of the second quasiequilibrium state let us take

$$v_{ik}=mv_iv_k,\quad i,k=1,2,3\,. \tag{36}$$

Then

$$(\hat{1}-\hat{P}^{(0)})v_{ik}=m(v_i-u_i)(v_k-u_k)-\tfrac{1}{3}\delta_{ik}m(\boldsymbol{v}-\boldsymbol{u})^2 \tag{37}$$

and, since $((\hat{1}-\hat{P}^{(0)})v_{ik},(\hat{1}-\hat{P}^{(0)})v_{ls})=(\delta_{il}\delta_{ks}+\delta_{kl}\delta_{is})Pk_{\mathrm{B}}T/m$, where $P=nk_{\mathrm{B}}T$ is the pressure, and $\sigma_{ik}=(f,(\hat{1}-\hat{P}^{(0)})v_{ik})$ is the traceless part of the stress tensor, then from (20), (33), (34), (37) we obtain the distribution function of the second quasiequilibrium state in the form

$$f=f^{(0)}\left(1+\frac{\sigma_{ik}m}{2Pk_{\mathrm{B}}T}\left[(v_i-u_i)(v_k-u_k)-\frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2\right]\right)\,. \tag{38}$$

This is precisely the distribution function of the ten-moment Grad approximation (let us recall that here summation in two repeated indices is assumed).

3.3. Thirteen-moment Grad approximation

In addition to (33) and (36), let us extend the list of moment densities of the second quasiequilibrium state with the functions

$$\xi_i=\frac{mv_iv^2}{2},\quad i=1,2,3\,. \tag{39}$$

The corresponding orthogonal complements to the projection on the first quasiequilibrium state are

$$(\hat{1}-\hat{P}^{(0)})\xi_i = \frac{m}{2}(v_i-u_i)\left((\boldsymbol{v}-\boldsymbol{u})^2-\frac{5k_{\mathrm{B}}T}{m}\right). \tag{40}$$

The moments corresponding to the densities $(\hat{1}-\hat{P}^{(0)})\xi_i$ are the components of the heat flux vector q_i

$$q_i = (\varphi, (\hat{1}-\hat{P}^{(0)})\xi_i). \tag{41}$$

Since $((\hat{1}-\hat{P}^{(0)})\xi_i, (\hat{1}-\hat{P}^{(0)})v_{lk}) = 0$, for any i, k, l, then the constraints $((\hat{1}-\hat{P}^{(0)})v_{lk}, \varphi) = \sigma_{lk}, ((\hat{1}-\hat{P}^{(0)})\xi_i, \varphi) = q_i$ in problem (32) are independent, and Lagrange multipliers corresponding to ξ_i are

$$\frac{1}{5n}\left(\frac{k_{\mathrm{B}}T}{m}\right)^2 q_i. \tag{42}$$

Finally, taking into account (33), (38), (40), (42), we find the distribution function of the second quasiequilibrium state in the form

$$\begin{aligned} f = f^{(0)}\Bigg(1 &+ \frac{\sigma_{ik}m}{2Pk_{\mathrm{B}}T}\left((v_i-u_i)(v_k-u_k)-\frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2\right) \\ &+ \frac{q_i m}{Pk_{\mathrm{B}}T}(v_i-u_i)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{5k_{\mathrm{B}}T}-1\right)\Bigg) \end{aligned} \tag{43}$$

which coincides with the thirteen-moment Grad distribution function [19].

Let us remark on the thirteen-moment approximation. From (43) it follows that for large enough negative values of (v_i-u_i) the thirteen-moment distribution function becomes negative. This peculiarity of the thirteen-moment approximation is due to the fact that the moment density ξ_i is odd-order polynomial of v_i. In order to eliminate this difficulty, one may consider from the very beginning that in a finite volume the square of velocity of a particle does not exceed a certain value $v^2_{\max}$, which is finite owing to the finiteness of the total energy, and q_i is such that when changing to infinite volume $q_i \to 0$, $v^2_{\max} \to \infty$ and $q_i(v_i-u_i)(\boldsymbol{v}-\boldsymbol{u})^2$ remains finite.

On the other hand, the solution to the optimization problem (11) does not exist (is not normalizable), if the highest-order velocity polynomial is odd, as it is for the full 13-moment quasiequilibrium.

Approximation (38) yields ΔH (29) as follows:

$$\Delta H = H^{(0)} + n\frac{\sigma_{ik}\sigma_{ik}}{4P^2} \tag{44}$$

while ΔH corresponding to (43) is

$$\Delta H = H^{(0)} + n\frac{\sigma_{ik}\sigma_{ik}}{4P^2} + n\frac{q_k q_k \rho}{5P^3}, \tag{45}$$

where $\rho = mn$, and $H^{(0)}$ is the local equilibrium value of the H-function

$$H^{(0)} = \frac{5}{2}n\ln n - \frac{3}{2}n\ln P - \frac{3}{2}n\left(1+\ln\frac{2\pi}{m}\right). \tag{46}$$

These expressions coincide with the corresponding expansions of the quasiequilibrium H-functions obtained by the entropy method, if microscopic moment densities of the first quasiequilibrium approximation are chosen as $1, v_i$, and v_iv_j, or as $1, v_i$, v_iv_j, and v_iv^2. As it was noted in Ref. [6], they differ from the H-functions obtained by the Grad method (without the maximum entropy hypothesis), and in contrast to the latter they give proper entropy balance equations.

The transition to the closed system of equations for the moments of the first and of the second quasiequilibrium approximations is accomplished by proceeding from the chain of the Maxwell moment equations, which is equivalent to the Boltzmann equation. Substituting f in the form of $f^{(0)}(1+\varphi)$ into Eq. (7), and multiplying by $\mu_i(\boldsymbol{v})$, and integrating over $\boldsymbol{v}$, we obtain

$$\begin{aligned}&\partial_t(1, \hat{P}^{(0)}\mu_i(\boldsymbol{v})) + \partial_t(\varphi(\boldsymbol{v}), \mu_i(\boldsymbol{v})) + \partial_k(v_k\varphi(\boldsymbol{v}), \mu_i(\boldsymbol{v})) + \partial_k(v_k, \mu_i(\boldsymbol{v}))\\ &\quad = M_Q[\mu_i, \varphi]\,. \end{aligned} \tag{47}$$

Here, $M_Q[\mu_i, \varphi] = \int Q(f^{(0)}(1+\varphi), f^{(0)}(1+\varphi))\mu_i(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v}$ is a "moment" (corresponding to the microscopic density) $\mu_i(\boldsymbol{v})$ with respect to the collision integral (further we term M_Q the collision moment or the scattering rate). Now, if one uses f given by Eqs. (38) and (43) as a closure assumption, then system (47) gives the ten- and thirteen-moment Grad equations, respectively, whereas only linear terms in φ should be kept when calculating M_Q.

Let us note some limitations of truncating the moment hierarchy (47) by means of the quasiequilibrium distribution functions (38) and (43) (or for any other closure which depends on the moments of the distribution functions only). When such closure is used, it is assumed implicitly that the scattering rates in the right-hand side of (47) "rapidly" relax to their values determined by "slow" (quasiequilibrium) moments. Scattering rates are, generally speaking, independent variables. This peculiarity of the chain (47), resulting from the nonlinear character of the Boltzmann equation, distinct it essentially from the other hierarchy equations of statistical mechanics (for example, from the BBGKY chain which follows from the linear Liouville equation). Thus, Eq. (47) is not closed twice: into the left-hand side of the equation for the ith moment enters the $(i+1)$th moment, and the right-hand side contains additional variables—scattering rates. The TEM enables to address both sets of variables (moments and scattering rates) as independent variables.

4. Transport equations for scattering rates in the neighbourhood of local equilibrium. Second and mixed hydrodynamic chains

In this section we derive equations of motion for the scattering rates. It proves convenient to use the following form of the collision integral $Q(f,f)$:

$$Q(f,f)(\boldsymbol{v}) = \int w(\boldsymbol{v}'_1, v' \mid \boldsymbol{v}, v_1)\big(f(\boldsymbol{v}')f(\boldsymbol{v}'_1) - f(\boldsymbol{v})f(\boldsymbol{v}_1)\big)\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}'_1\,\mathrm{d}\boldsymbol{v}_1\,, \tag{48}$$

where $\boldsymbol{v}$ and $\boldsymbol{v}_1$ are velocities of the two colliding particles before the collision, $\boldsymbol{v}'$ and $\boldsymbol{v}'_1$ are their velocities after the collision, w is a kernel responsible for the post-collision relations $\boldsymbol{v}'(\boldsymbol{v},\boldsymbol{v}_1)$ and $\boldsymbol{v}_1'(\boldsymbol{v},\boldsymbol{v}_1)$, momentum and energy conservation laws are taken into account in w by means of corresponding δ-functions. The kernel w has the following symmetry property with respect to its arguments:

$$w(\boldsymbol{v}_1',\boldsymbol{v}' \mid \boldsymbol{v},\boldsymbol{v}_1) = w(\boldsymbol{v}_1',\boldsymbol{v}' \mid \boldsymbol{v}_1,\boldsymbol{v}) = w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v}_1,\boldsymbol{v}) = w(\boldsymbol{v},\boldsymbol{v}_1 \mid \boldsymbol{v}',\boldsymbol{v}_1') \,. \tag{49}$$

Let $\mu(\boldsymbol{v})$ be the microscopic density of a moment M. The corresponding scattering rate $M_Q[f,\mu]$ is defined as follows:

$$M_Q[f,\mu] = \int Q(f,f)(\boldsymbol{v})\mu(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} \,. \tag{50}$$

First, we should obtain transport equations for scattering rates (50), analogous to the moment's transport equations. Let us restrict ourselves to the case when f is represented in the form

$$f = f^{(0)}(1+\varphi) \,, \tag{51}$$

where $f^{(0)}$ is local Maxwell distribution function (34), and all the quadratic with respect to φ terms will be neglected below. It is the linear approximation around the local equilibrium.

Since, by detailed balance

$$f^{(0)}(\boldsymbol{v})f^{(0)}(\boldsymbol{v}_1) = f^{(0)}(\boldsymbol{v}')f^{(0)}(\boldsymbol{v}_1') \tag{52}$$

for all such ($\boldsymbol{v}$, $\boldsymbol{v}_1$), ($\boldsymbol{v}'$, $\boldsymbol{v}_1'$) which are related to each other by conservation laws, we have

$$M_Q[f^{(0)},\mu] = 0 \quad \text{for any } \mu \,. \tag{53}$$

Further, by virtue of conservation laws

$$M_Q[f,\hat{P}^{(0)}\mu] = 0 \quad \text{for any } f \,. \tag{54}$$

From (52)–(54) it follows

$$\begin{aligned} &M_Q[f^{(0)}(1+\varphi),\mu] \\ &\quad = M_Q[\varphi,(\hat{1}-\hat{P}^{(0)})\mu] \\ &\quad = -\int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v})f^{(0)}(\boldsymbol{v}_1)\{(1-\hat{P}^{(0)})\mu(\boldsymbol{v})\}\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}_1\,\mathrm{d}\boldsymbol{v} \,. \end{aligned} \tag{55}$$

We used notation

$$\{\psi(\boldsymbol{v})\} = \psi(\boldsymbol{v}) + \psi(\boldsymbol{v}_1) - \psi(\boldsymbol{v}') - \psi(\boldsymbol{v}_1') \,. \tag{56}$$

Also, it proves convenient to introduce the microscopic density of the scattering rate, $\mu_Q(\boldsymbol{v})$:

$$\mu_Q(\boldsymbol{v}) = \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v}_1)\Big\{(1-\hat{P}^{(0)})\mu(\boldsymbol{v})\Big\}\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}_1 \,. \tag{57}$$

Then

$$M_Q[\varphi,\mu] = -(\varphi,\mu_Q) \,, \tag{58}$$

where $(\cdot,\cdot)$ is the L_2 scalar product with the weight $f^{(0)}$ (34). This is a natural scalar product in the space of functions φ (51) (multipliers), and it is obviously related to the entropic scalar product in the space of distribution functions at the local equilibrium $f^{(0)}$, which is the L_2 scalar product with the weight $(f^{(0)})^{-1}$.

Now, we obtain transport equations for the scattering rates (58). We write down the time derivative of the collision integral due to the Boltzmann equation

$$\partial_t Q(f,f)(\boldsymbol{v}) = \hat{T}\mathrm{Q}(f,f)(\boldsymbol{v}) + \hat{R}\mathrm{Q}(f,f)(\boldsymbol{v})\,, \tag{59}$$

where

$$\begin{aligned}\hat{T}Q(f,f)(\boldsymbol{v}) = \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)[&f(\boldsymbol{v})v_{1k}\partial_k f(\boldsymbol{v}_1) + f(\boldsymbol{v}_1)v_k\partial_k f(\boldsymbol{v}) \\ &- f(\boldsymbol{v}')v_{1k}'\partial_k f(\boldsymbol{v}_1') - f(\boldsymbol{v}_1')v_k'\partial_k f(\boldsymbol{v}')\big]\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}_1\,\mathrm{d}\boldsymbol{v}\,,\end{aligned} \tag{60}$$

$$\begin{aligned}\hat{R}Q(f,f)(\boldsymbol{v}) = \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)\big[&Q(f,f)(\boldsymbol{v}')f(\boldsymbol{v}_1') + Q(f,f)(\boldsymbol{v}_1')f(\boldsymbol{v}') \\ &- Q(f,f)(\boldsymbol{v}_1)f(\boldsymbol{v}) - Q(f,f)(\boldsymbol{v})f(\boldsymbol{v}_1)]\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}_1\,\mathrm{d}\boldsymbol{v}\,.\end{aligned} \tag{61}$$

Using the representation

$$\begin{aligned}&\partial_k f^{(0)}(\boldsymbol{v}) = A_k(\boldsymbol{v})f^{(0)}(\boldsymbol{v})\,,\\ &A_k(\boldsymbol{v}) = \partial_k \ln(nT^{-3/2}) + \frac{m}{k_{\mathrm{B}}T}(v_i - u_i)\partial_k u_i + \frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\partial_k \ln T\end{aligned} \tag{62}$$

and after some simple transformations using the relation

$$\big\{A_k(\boldsymbol{v})\big\} = 0 \tag{63}$$

in linear with respect to φ deviation from $f^{(0)}$ (51), we obtain in (59)

$$\begin{aligned}\hat{T}Q(f,f)(\boldsymbol{v}) = \partial_k &\int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v})\big\{v_k\varphi(\boldsymbol{v})\big\}\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1\\ &+ \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v})\big\{v_kA_k(\boldsymbol{v})\big\}\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}_1\\ &+ \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v})f^{(0)}(\boldsymbol{v}_1)\big[\varphi(\boldsymbol{v})A_k(\boldsymbol{v}_1)(v_{1k}-v_k)\\ &+ \varphi(\boldsymbol{v}_1)A_k(\boldsymbol{v})(v_k - v_{1k}) + \varphi(\boldsymbol{v}')A_k(\boldsymbol{v}_1')(v_k' - v_{1k}')\\ &+ \varphi(\boldsymbol{v}_1')A_k(\boldsymbol{v}')(v_{1k}' - v_k')\big]\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1\,,\end{aligned} \tag{64}$$

$$\begin{aligned}\hat{R}Q(f,f)(\boldsymbol{v}) &= \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v})f^{(0)}(\boldsymbol{v}_1)\big\{\xi(\boldsymbol{v})\big\}\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1\,,\\ \xi(\boldsymbol{v}) &= \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v}_1)\big\{\varphi(\boldsymbol{v})\big\}\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1\,,\end{aligned} \tag{65}$$

$$\partial_t Q(f,f)(\boldsymbol{v}) = -\partial_t \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1)f^{(0)}(\boldsymbol{v})f^{(0)}(\boldsymbol{v}_1)\big\{\varphi(\boldsymbol{v})\big\}\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}_1\,. \tag{66}$$

Let us use two identities:

1. From the conservation laws it follows

$$\left\{\varphi(\boldsymbol{v})\right\} = \{(\hat{1} - \hat{P}^{(0)})\varphi(\boldsymbol{v})\}\,. \tag{67}$$

2. The symmetry property of the kernel w (49) which follows from (49), (52)

$$\begin{aligned}&\int w(\boldsymbol{v}', \boldsymbol{v}_1' \mid \boldsymbol{v}, \boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) g_1(\boldsymbol{v})\{g_2(\boldsymbol{v})\}\, \mathrm{d}\boldsymbol{v}'\, \mathrm{d}\boldsymbol{v}_1'\, \mathrm{d}\boldsymbol{v}_1\, \mathrm{d}\boldsymbol{v} \\ &\quad = \int w(\boldsymbol{v}', \boldsymbol{v}_1' \mid \boldsymbol{v}, \boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) g_2(\boldsymbol{v})\{g_1(\boldsymbol{v})\}\, \mathrm{d}\boldsymbol{v}'\, \mathrm{d}\boldsymbol{v}_1'\, \mathrm{d}\boldsymbol{v}_1\, \mathrm{d}\boldsymbol{v}\,. \end{aligned} \tag{68}$$

It is valid for any two functions g_1, g_2 ensuring existence of the integrals, and also using the first identity.

Now, multiplying (64)–(67) by the microscopic moment density $\mu(\boldsymbol{v})$, performing integration over $\boldsymbol{v}$ (and using identities (67), (69)) we obtain the required transport equation for the scattering rate in the linear neighborhood of the local equilibrium:

$$\begin{aligned} -\partial_t \Delta M_Q[\varphi, \mu] \equiv\ & -\partial_t(\varphi, \mu_Q) \\ &= (v_k A_k(\boldsymbol{v}), \mu_Q((\hat{1} - \hat{P}^{(0)})\mu(\boldsymbol{v}))) + \partial_k(\varphi(\boldsymbol{v}) v_k, \mu_Q((\hat{1} - \hat{P}^{(0)})\mu(\boldsymbol{v}))) \\ &\quad + \int w(\boldsymbol{v}', \boldsymbol{v}_1' \mid \boldsymbol{v}, \boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) \\ &\quad \times \left\{(\hat{1} - \hat{P}^{(0)})\mu(\boldsymbol{v})\right\} A_k(\boldsymbol{v}_1)(v_{1k} - v_k)\varphi(\boldsymbol{v})\, \mathrm{d}\boldsymbol{v}'\, \mathrm{d}\boldsymbol{v}_1'\, \mathrm{d}\boldsymbol{v}_1 d\boldsymbol{v} \\ &\quad + (\xi(\boldsymbol{v}), \mu_Q((\hat{1} - \hat{P}^{(0)})\mu(\boldsymbol{v})))\,. \end{aligned} \tag{69}$$

The chain of equations (69) for scattering rates is a counterpart of the hydrodynamic moment chain (47). Below we call (69) the *second chain*, and (47)—the *first chain*. Equations of the second chain are coupled in the same way as the first one: the last term in the right part of (69) $(\xi, \mu_Q((\hat{1} - \hat{P}^{(0)})\mu))$ depends on the whole totality of moments and scattering rates and may be treated as a new variable. Therefore, generally speaking, we have an infinite sequence of chains of increasingly higher orders. Only in the case of a special choice of the collision model—Maxwell potential $U = -\kappa r^{-4}$—this sequence degenerates: the second and the higher-order chains are equivalent to the first (see below).

Let us restrict our consideration to the first and second hydrodynamic chains. Then a deviation from the local equilibrium state and transition to a closed macroscopic description may be performed in three different ways for the microscopic moment density $\mu(\boldsymbol{v})$. First, one can specify the moment $\hat{M}[\mu]$ and perform a closure of the chain (47) by the triangle method given in previous subsections. This leads to Grad's moment method. Second, one can specify scattering rate $\hat{M}_Q[\mu]$ and perform a closure of the second hydrodynamic chain (69). Finally, one can consider simultaneously both $\hat{M}[\mu]$ and $\hat{M}_Q[\mu]$ (mixed chain). Quasiequilibrium distribution functions corresponding to the last two variants will be constructed in the following subsection. The hard sphere model (H.S.) and Maxwell's molecules (M.M.) will be considered.

5. Distribution functions of the second quasiequilibrium approximation for scattering rates

5.1. First five moments and collision stress tensor

Elsewhere below the local equilibrium $f^{(0)}$ (34) is chosen as the first quasiequilibrium approximation.

Let us choose $\nu_{ik} = mv_iv_k$ (36) as the microscopic density $\mu(\boldsymbol{v})$ of the second quasiequilibrium state. Let us write down the corresponding scattering rate (collision stress tensor) Δ_{ik} in the form

$$\Delta_{ik} = -(\varphi, \nu_{Qik})\,, \tag{70}$$

where

$$\begin{aligned}\nu_{Qik}(\boldsymbol{v}) = m \int & w(\boldsymbol{v}', \boldsymbol{v}_1' \mid \boldsymbol{v}_1, \boldsymbol{v}) f^{(0)}(\boldsymbol{v}_1) \\ & \times \left\{ (v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v} - \boldsymbol{u})^2 \right\} \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{v}_1' \, \mathrm{d}\boldsymbol{v}_1\end{aligned} \tag{71}$$

is the microscopic density of the scattering rate Δ_{ik}.

The quasiequilibrium distribution function of the second quasiequilibrium approximation for fixed scattering rates (70) is determined as the solution to the problem

$$(\varphi, \varphi) \to \min \quad \text{for } (\varphi, \nu_{Qik}) = -\Delta_{ik}\,. \tag{72}$$

The method of Lagrange multipliers yields

$$\varphi(\boldsymbol{v}) = \lambda_{ik}\nu_{Qik}(\boldsymbol{v}), \quad \lambda_{ik}(\nu_{Qik}, \nu_{Qls}) = \Delta_{ls}\,, \tag{73}$$

where λ_{ik} are the Lagrange multipliers.

In the examples of collision models considered below (and in general, for spherically symmetric interactions) ν_{Qik} is of the form

$$\nu_{Qik}(\boldsymbol{v}) = (\hat{1} - \hat{P}^{(0)})\nu_{ik}(\boldsymbol{v})\Phi((\boldsymbol{v} - \boldsymbol{u})^2)\,, \tag{74}$$

where $(\hat{1} - \hat{P}^{(0)})\nu_{ik}$ is determined by relationship (37) only, and function Φ depends only on the absolute value of the peculiar velocity $(\boldsymbol{v} - \boldsymbol{u})$. Then

$$\begin{aligned}&\lambda_{ik} = r\Delta_{ik}\,, \\ &r^{-1} = (2/15)\left(\Phi^2((\boldsymbol{v} - \boldsymbol{u})^2), (\boldsymbol{v} - \boldsymbol{u})^4\right)\end{aligned} \tag{75}$$

and the distribution function of the second quasiequilibrium approximation for scattering rates (70) is given by the expression of the form

$$f = f^{(0)}(1 + r\Delta_{ik}\mu_{Qik})\,. \tag{76}$$

The form of the function $\Phi((\boldsymbol{v} - \boldsymbol{u})^2)$, and the value of the parameter r are determined by the model of particle's interaction. In the Appendix A, they are found for hard sphere and Maxwell molecules models (see (134)–(139)). The distribution function (76) is given by the following expressions:

For Maxwell molecules:

$$f = f^{(0)}\left\{1 + \mu_0^{\mathrm{M.M.}} m(2P^2 k_{\mathrm{B}}T)^{-1}\Delta_{ik}\left((v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v} - \boldsymbol{u})^2\right)\right\},$$

$$\mu_0^{\mathrm{M.M.}} = \frac{k_{\mathrm{B}}T\sqrt{2m}}{3\pi A_2(5)\sqrt{\kappa}}, \tag{77}$$

where $\mu_0^{\mathrm{M.M.}}$ is viscosity coefficient in the first approximation of the Chapman–Enskog method (it is exact in the case of Maxwell molecules), κ is a force constant, $A_2(5)$ is a number, $A_2(5) \approx 0.436$ (see Ref. [33]).

For the hard sphere model

$$\begin{aligned} f &= f^{(0)} \\ &\times \left\{1 + \frac{2\sqrt{2}\tilde{r}m\mu_0^{\mathrm{H.S.}}}{5P^2 k_{\mathrm{B}}T}\Delta_{ik}\int_{+1}^{-1}\exp\left\{-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right\}(1-y^2)(1+y^2)\right. \\ &\left.\times \left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}(1-y^2) + 2\right)\mathrm{d}y\left((v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2\right)\right\}, \end{aligned}$$

$$\mu_0^{\mathrm{H.S.}} = (5\sqrt{k_{\mathrm{B}}Tm})/(16\sqrt{\pi}\sigma^2), \tag{78}$$

where $\tilde{r}$ is a number represented as follows:

$$\begin{aligned} \tilde{r}^{-1} &= \frac{1}{16}\int_{-1}^{+1}\int_{-1}^{+1}\alpha^{-11/2}\beta(y)\beta(z)\gamma(y)\gamma(z) \\ &\quad\times(16\alpha^2 + 28\alpha(\gamma(y)+\gamma(z)) + 63\gamma(y)\gamma(z))\,\mathrm{d}y\,\mathrm{d}z, \\ \alpha &= 1 + y^2 + z^2, \quad \beta(y) = 1 + y^2, \quad \gamma(y) = 1 - y^2. \end{aligned} \tag{79}$$

Numerical value of $\tilde{r}^{-1}$ is 5.212, to third decimal point accuracy.

In the mixed description, the distribution function of the second quasiequilibrium approximation under fixed values of the moments and of the scattering rates corresponding to the microscopic density (36) is determined as a solution of the problem

$$(\varphi, \varphi) \to \min \quad \text{for } ((\hat{1} - \hat{P}^{(0)})v_{ik}, \varphi) = \sigma_{ik}, \quad (v_{Qik}, \varphi) = \Delta_{ik}. \tag{80}$$

Taking into account relation (74), we obtain the solution of problem (80) in the form

$$\varphi(\boldsymbol{v}) = (\lambda_{ik}\Phi((\boldsymbol{v}-\boldsymbol{u})^2) + \beta_{ik})((v_i - u_i)(v_k - u_k) - (1/3)\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2). \tag{81}$$

Lagrange multipliers λ_{ik}, β_{ik} are determined from the system of linear equations

$$ms^{-1}\lambda a_{ik} + 2Pk_{\mathrm{B}}Tm^{-1}\beta_{ik} = \sigma_{ik}, \quad mr^{-1}\lambda_{ik} + ms^{-1}\beta_{ik} = \Delta_{ik}, \tag{82}$$

where

$$s^{-1} = (2/15)(\Phi((\boldsymbol{v}-\boldsymbol{u})^2), (\boldsymbol{v}-\boldsymbol{u})^4). \tag{83}$$

If the solvability condition of system (82) is satisfied

$$D = m^2 s^{-2} - 2Pk_{\mathrm{B}}Tr^{-1} \neq 0\,, \tag{84}$$

then the distribution function of the second quasiequilibrium approximation exists and takes the form

$$\begin{aligned} f = f^{(0)}\{1 &+ (m^2 s^{-2} - 2Pk_{\mathrm{B}}Tr^{-1})^{-1}[(ms^{-1}\sigma_{ik} - 2Pk_{\mathrm{B}}Tm^{-1}\Delta_{ik})\Phi((\boldsymbol{v}-\boldsymbol{u})^2) \\ &+ (ms^{-1}\Delta_{ik} - mr^{-1}\sigma_{ik})]((v_i - u_i)(v_k - u_k) - (1/3)\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2)\}\,. \end{aligned} \tag{85}$$

Condition (84) means independence of the set of moments σ_{ik} from the scattering rates Δ_{ik}. If this condition is not satisfied, then the scattering rates Δ_{ik} can be represented in the form of linear combinations of σ_{ik} (with coefficients depending on the hydrodynamic moments). Then the closed by means of (76) equations of the second chain are equivalent to the ten moment Grad equations, while the mixed chain does not exist. This happens only in the case of Maxwell molecules. Indeed, in this case $s^{-1} = 2P^2k_{\mathrm{B}}T(m^2\mu_0^{\mathrm{M.M.}})^{-1}; D = 0$. The transformation changing Δ_{ik} to σ_{ik} is

$$\mu_0^{\mathrm{M.M.}}\Delta_{ik}P^{-1} = \sigma_{ik}\,. \tag{86}$$

For hard spheres:

$$s^{-1} = \frac{5P^2k_{\mathrm{B}}T}{4\sqrt{2}\mu_0^{\mathrm{H.S.}}m^2}\cdot\tilde{s}^{-1}, \quad \tilde{s}^{-1} = \int_{-1}^{+1}\gamma(y)(\beta(y))^{-7/2}\left(\beta(y) + \frac{7}{4}\gamma(y)\right)\mathrm{d}y\,. \tag{87}$$

The numerical value of $\tilde{s}^{-1}$ is 1.115 to third decimal point. The condition (83) takes the form

$$D = \frac{25}{32}\left(\frac{P^2k_{\mathrm{B}}T}{m\mu_0^{\mathrm{H.S.}}}\right)^2(\tilde{s}^{-2} - \tilde{r}^{-1}) \neq 0\,. \tag{88}$$

Consequently, for the hard sphere model the distribution function of the second quasiequilibrium approximation of the mixed chain exists and is determined by the expression

$$\begin{aligned} f = f^{(0)}\Bigg\{&1 + m(4Pk_{\mathrm{B}}T(\tilde{s}^{-2} - \tilde{r}^{-1}))^{-1} \\ &\times\left[\left(\sigma_{ik}\tilde{s}^{-1} - \frac{8\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\Delta_{ik}\right)\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\right. \\ &\times(1-y^2)(1+y^2)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}(1-y^2) + 2\right)\mathrm{d}y \\ &\left.+ 2\left(\tilde{s}^{-1}\cdot\frac{8\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\Delta_{ik} - \tilde{r}^{-1}\sigma_{ik}\right)\right] \\ &\times\left((v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2\right)\Bigg\}\,. \end{aligned} \tag{89}$$

5.2. First five moments, collision stress tensor, and collision heat flux vector

Distribution function of the second quasiequilibrium approximation which takes into account the collision heat flux vector Q is constructed in a similar way. The microscopic density ξ_{Qi} is

$$\xi_{Qi}(\boldsymbol{v}) = \int w(\boldsymbol{v}', \boldsymbol{v}'_1 \mid \boldsymbol{v}, \boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) \left\{ (\hat{1} - \hat{P}^{(0)}) \frac{v_i^2 v}{2} \right\} \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{v}'_1 \, \mathrm{d}\boldsymbol{v}_1 \, . \tag{90}$$

The desired distribution functions are the solutions to the following optimization problems: for the second chain it is the solution to problem (72) with the additional constraints

$$m(\varphi, \xi_{Qi}) = Q_i \, . \tag{91}$$

For the mixed chain, the distribution functions is the solution to problem (80) with additional conditions

$$m(\varphi, \xi_{Qi}) = Q_i, \quad m(\varphi, (\hat{1} - \hat{P}^{(0)})\xi_i) = q_i \, . \tag{92}$$

Here $\xi_i = v_i v^2/2$ (see (39)). In Appendix A functions ξ_{Qi} are found for Maxwell molecules and hard spheres (see (139)–(144)). Since

$$\begin{aligned}(\xi_{Qi}, v_{Qkj}) &= ((\hat{1} - \hat{P}^{(0)})\xi_i, v_{Qkj}) \\ &= (\xi_{Qi}, (\hat{1} - \hat{P}^{(0)})v_{kj}) = ((\hat{1} - \hat{P}^{(0)})\xi_i, (\hat{1} - \hat{P}^{(0)})v_{kj}) = 0\end{aligned} \tag{93}$$

conditions (91) are linearly independent from the constraints of problem (72), and conditions (92) do not depend on the constraints of problem (80).

Distribution function of the second quasiequilibrium approximation of the second chain for fixed Δ_{ik}, Q_i is of the form

$$f = f^{(0)}(1 + r\Delta_{ik} v_{Qik} + \eta Q_i \xi_{Qi}) \, . \tag{94}$$

The parameter η is determined by the relation

$$\eta^{-1} = (1/3)(\xi_{Qi}, \xi_{Qi}) \, . \tag{95}$$

According to (143), for Maxwell molecules

$$\eta = \frac{9m^3(\mu_0^{\mathrm{M.M.}})^2}{10P^3(k_{\mathrm{B}}T)^2} \tag{96}$$

and the distribution function (94) is

$$\begin{aligned} f = f^{(0)}\Big\{ & 1 + \mu_0^{\mathrm{M.M.}} m(2P^2 k_{\mathrm{B}} T)^{-1} \Delta_{ik}((v_i - u_i)(v_k - u_k) \\ & - \frac{1}{3}\delta_{ik}(\boldsymbol{v} - \boldsymbol{u})^2) + \mu_0^{\mathrm{M.M.}} m(P^2 k_{\mathrm{B}} T)^{-1}(v_i - u_i)\left(\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{5k_{\mathrm{B}}T} - 1\right)\Big\} \, . \end{aligned} \tag{97}$$

For hard spheres (see Appendix A)

$$\eta = \tilde{\eta}\frac{64m^3(\mu_0^{\mathrm{H.S.}})^2}{125P^3(k_{\mathrm{B}}T)^2}\,, \tag{98}$$

where η is a number equal to 16.077 to third decimal point accuracy.

The distribution function (94) for hard spheres takes the form

$$\begin{aligned} f = f^{(0)}\Bigg\{ & 1 + \frac{2\sqrt{2}\tilde{r}m\mu_0^{\mathrm{H.S.}}}{5P^2k_{\mathrm{B}}T}\Delta_{ik}\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\beta(y)\gamma(y) \\ & \times\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\gamma(y)+2\right)\mathrm{d}y\left((v_i-u_i)(v_k-u_k)-\frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2\right) \\ & + \frac{2\sqrt{2}\tilde{\eta}m^3\mu_0^{\mathrm{H.S.}}}{25P^2(k_{\mathrm{B}}T)^2}Q_i\Bigg[(v_i-u_i)\left((\boldsymbol{v}-\boldsymbol{u})^2-\frac{5k_{\mathrm{B}}T}{m}\right) \\ & \times\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\beta(y)\gamma(y)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\gamma(y)+2\right)\mathrm{d}y \\ & + (v_i-u_i)(\boldsymbol{v}-\boldsymbol{u})^2\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\beta(y)\gamma(y) \\ & \times\left(\sigma(y)\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}+\delta(y)\right)\mathrm{d}y\Bigg]\Bigg\}\,. \end{aligned} \tag{99}$$

The functions $\beta(y), \gamma(y), \sigma(y)$ and $\delta(y)$ are

$$\beta(y) = 1+y^2,\quad \gamma(y) = 1-y^2,\quad \sigma(y) = y^2(1-y^2),\quad \delta(y) = 3y^2-1\,. \tag{100}$$

The condition of existence of the second quasiequilibrium approximation of the mixed chain (84) should be supplemented with the requirement

$$R = m^2\tau^{-2} - \frac{5P(k_{\mathrm{B}}T)^2}{2m}\eta^{-1} \neq 0\,. \tag{101}$$

Here

$$\tau^{-1} = \frac{1}{3}\left((\hat{1}-\hat{P}^{(0)})\frac{v_i^2 v}{2}, \xi_{Qi}(\boldsymbol{v})\right)\,. \tag{102}$$

For Maxwell molecules $\tau^{-1} = (5P^2k_{\mathrm{B}}^2T^2)/(3\mu_0^{\mathrm{M.M.}}m^3)$, and the solvability condition (101) is not satisfied. Distribution function of the second quasiequilibrium approximation of mixed chain does not exist for Maxwell molecules. The variables Q_i are changed to q_i by the transformation

$$3\mu_0^{\mathrm{M.M.}}Q_i = 2Pq_i\,. \tag{103}$$

For hard spheres

$$\tau^{-1} = \tilde{\tau}^{-1} = \frac{25(Pk_{\mathrm{B}}T)^2}{8\sqrt{2}m^3\mu_0^{\mathrm{H.S.}}}\,, \tag{104}$$

where

$$\tilde{\tau}^{-1} = \frac{1}{8}\int_{-1}^{+1} \beta^{-9/2}(y)\gamma(y)\{63(\gamma(y)+\sigma(y)) + 7\beta(y)(4-10\gamma(y)+2\delta(y)-5\sigma(y)) + \beta^2(y)(25\gamma(y)-10\delta(y)-40) + 20\beta^3(y)\}\,\mathrm{d}y\,. \tag{105}$$

The numerical value of $\tilde{\tau}^{-1}$ is about 4.322. Then condition (101) is verified: $R \approx 66m^{-4}(Pk_{\mathrm{B}}T)^4(\mu_0^{\mathrm{H.S.}})^2$. Finally, for the fixed values of $\sigma_{ik}, \Delta_{ik}, q_i$ and Q_i the distribution function of the second quasiequilibrium approximation of the second chain for hard spheres is of the form

$$\begin{aligned}
f = f^{(0)}\Bigg\{ & 1 + \frac{m}{4Pk_{\mathrm{B}}T}(\tilde{s}^{-2}-\tilde{r}^{-1})^{-1} \\
& \times \left[\left(\tilde{s}^{-1}\sigma_{ik} - \frac{8\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\Delta_{ik}\right)\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\right. \\
& \times \left.\beta(y)\gamma(y)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\gamma(y)+2\right)\mathrm{d}y + 2\left(\tilde{s}^{-1}\frac{8\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\Delta_{ik} - \tilde{r}^{-1}\sigma_{ik}\right)\right] \\
& \times \left((v_i-u_i)(v_k-u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2\right) \\
& + \frac{m^2}{10(Pk_{\mathrm{B}}T)^2}(\tilde{\tau}^{-2}-\tilde{\eta}^{-1})^{-1}\left[\left(\tilde{\tau}^{-1}q_i - \frac{4\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}Q_i\right)\right. \\
& \times \left((v_i-u_i)\left((\boldsymbol{v}-\boldsymbol{u})^2 - \frac{5k_{\mathrm{B}}T}{m}\right)\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\right. \\
& \times \beta(y)\gamma(y)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\gamma(y)+2\right)\mathrm{d}y + (v_i-u_i)(\boldsymbol{v}-\boldsymbol{u})^2 \\
& \times \left.\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\beta(y)\gamma(y)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\sigma(y)+\delta(y)\right)\mathrm{d}y\right) \\
& + 2\left.\left(\frac{4\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\tilde{\tau}^{-1}Q_i - \tilde{\eta}^{-1}q_i\right)(v_i-u_i)\left((\boldsymbol{v}-\boldsymbol{u})^2 - \frac{5k_{\mathrm{B}}T}{m}\right)\right]\Bigg\}\,.
\end{aligned} \tag{106}$$

Thus, expressions (77), (78), (89), (97), (99) and (106) give distribution functions of the second quasiequilibrium approximation of the second and mixed hydrodynamic chains for Maxwell molecules and hard spheres. They are analogues of ten- and thirteen-moment Grad approximations (38), (42). The next step is to close the second and mixed hydrodynamic chains by means of the found distribution functions.

6. Closure of the second chain for Maxwell molecules

6.1. Second chain, Maxwell molecules

The distribution function of the second quasiequilibrium approximation under fixed Δ_{ik} for Maxwell molecules (77) presents the simplest example of the closure of the first (47) and second (69) hydrodynamic chains. With the help of it, we obtain from (47) the following transport equations for the moments of the first (local equilibrium) approximation:

$$\partial_t\rho+\partial_i(u_i\rho)=0,\quad \rho(\partial_t u_k+u_i\partial_i u_k)+\partial_k P+\partial_i(P^{-1}\mu_0^{\mathrm{M.M.}}\Delta_{ik})=0\,,$$
$$\tfrac{3}{2}(\partial_t P+u_i\partial_i P)+\tfrac{5}{2}P\partial_i u_i+P^{-1}\mu_0^{\mathrm{M.M.}}\Delta_{ik}\partial_i u_k=0\,. \tag{107}$$

Now, let us from the scattering rate transport chain (69) find an equation for Δ_{ik} which closes the system (70). Substituting (77) into (69), we obtain after some computation

$$\begin{aligned}&\partial_t\Delta_{ik}+\partial_s(u_s\Delta_{ik})+\Delta_{is}\partial_s u_k+\Delta_{ks}\partial_s u_i-\tfrac{2}{3}\delta_{ik}\Delta_{ls}\partial_s u_l\\&\quad+P^2(\mu_0^{\mathrm{M.M.}})^{-1}\left(\partial_i u_k+\partial_k u_i-\tfrac{2}{3}\delta_{ik}\partial_s u_s\right)\\&\quad+P(\mu_0^{\mathrm{M.M.}})^{-1}\Delta_{ik}+\Delta_{ik}\partial_s u_s=0\,.\end{aligned} \tag{108}$$

For comparison, let us give ten-moment Grad equations obtained when closing the chain (47) by the distribution functions (38)

$$\partial_t\rho+\partial_i(u_i\rho)=0,\quad \rho(\partial_t u_k+u_i\partial_i u_k)+\partial_k P+\partial_i\sigma_{ik}=0\,,$$
$$\tfrac{3}{2}(\partial_t P+u_i\partial_i P)+\tfrac{5}{2}P\partial_i u_i+\sigma_{ik}\partial_i u_k=0\,, \tag{109}$$

$$\begin{aligned}&\partial_t\sigma_{ik}+\partial_s(u_s\sigma_{ik})+P\left(\partial_i u_k+\partial_k u_i-\tfrac{2}{3}\delta_{ik}\partial_s u_s\right)\\&\quad+\sigma_{is}\partial_s u_k+\sigma_{ks}\partial_s u_i-\tfrac{2}{3}\delta_{ik}\sigma_{ls}\partial_s u_l+P(\mu_0^{\mathrm{M.M.}})^{-1}\sigma_{ik}=0\,.\end{aligned} \tag{110}$$

Using the explicit form of $\mu_0^{\mathrm{M.M.}}$ (77), it is easy to verify that the transformation (86) maps systems (107), (108) and (109) into one another. This is a consequence of the degeneration of the mixed hydrodynamic chain which was already discussed. Systems (107), (108) and (109) are essentially equivalent. These specific properties of Maxwell molecules result from the fact that for them the microscopic densities $(\hat{1}-\hat{P}^{(0)})v_iv_k$ and $(\hat{1}-\hat{P}^{(0)})v_iv^2$ are eigen functions of the linearized collision integral.

7. Closure of the second chain for hard spheres and a "new determination of molecular dimensions" (revisited)

Here we apply the method developed in the previous sections to a classical problem: determination of molecular dimensions (as diameters of equivalent hard spheres) from experimental viscosity data. Same as in the previous section, we shall restrict ourselves to the truncation of the second chain at the level of ten moment approximation. After the chain of equations is closed with the functions $f^*(\rho,\boldsymbol{u},P,\Delta_{ij})$, we arrive at a set of equations with respect to the variables ρ, $\boldsymbol{u}$,P, and Δ_{ij}.

Expressions (70), (71), (74) for Δ_{ij} may be rewritten in the dimensionless form

$$\zeta_{ij}(\varphi)=n^{-1}\Delta_{ij}(\varphi)=\frac{P}{n\mu_0^{Q}(T)}\int S_Q(c^2)\left\{c_ic_j-\frac{1}{3}\delta_{ij}c^2\right\}f_0\varphi\,\mathrm{d}\boldsymbol{v}\,. \tag{111}$$

Here, μ_0^Q is the first Sonine polynomial approximation of the viscosity coefficient (VC) [33] (see, for example, (77), (78)), and, as usual, $\mathbf{c} = \sqrt{\frac{m}{2kT}}(\boldsymbol{v} - \boldsymbol{u})$. The scalar dimensionless function S_Q depends only on c^2, and its form depends on the choice of interaction w. In these variables, we have

$$\partial_t n + \partial_i(nu_i) = 0 \,, \tag{112}$$

$$\rho(\partial_t u_k + u_i\partial_i u_k) + \partial_k P + \partial_i\left\{\frac{\mu_0^Q(T)n}{2r_Q P}\zeta_{ik}\right\} = 0 \,, \tag{113}$$

$$\frac{3}{2}(\partial_t P + u_i\partial_i P) + \frac{5}{2}P\partial_i u_i + \left\{\frac{\mu_0^Q(T)n}{2r_Q P}\zeta_{ik}\right\}\partial_i u_k = 0 \,, \tag{114}$$

$$\begin{aligned}
&\partial_t\zeta_{ik} + \partial_s(u_s\zeta_{ik}) + \left\{\zeta_{ks}\partial_s u_i + \zeta_{is}\partial_s u_k - \frac{2}{3}\delta_{ik}\zeta_{rs}\partial_s u_r\right\}\\
&\quad + \left\{\gamma_Q - \frac{2\beta_Q}{r_Q}\right\}\zeta_{ik}\partial_s u_s - \frac{P^2}{\mu_0^Q(T)n}\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right)\\
&\quad - \frac{\alpha_Q P}{r_Q\mu_0^Q(T)}\zeta_{ik} = 0 \,.
\end{aligned} \tag{115}$$

Here, $\partial_t = \partial/\partial t, \partial_i = \partial/\partial x_i$, summation in two repeated indices is assumed, and the coefficients r_Q, β_Q, and α_Q are defined with the help of the function S_Q (111) as follows:

$$\begin{aligned}
r_Q &= \frac{8}{15\sqrt{\pi}}\int_0^\infty e^{-c^2}c^6\left(S_Q(c^2)\right)^2 \mathrm{d}c \,,\\
\beta_Q &= \frac{8}{15\sqrt{\pi}}\int_0^\infty e^{-c^2}c^6 S_Q(c^2)\frac{\mathrm{d}S_Q(c^2)}{\mathrm{d}(c^2)}\mathrm{d}c \,,\\
\alpha_Q &= \frac{8}{15\sqrt{\pi}}\int_0^\infty e^{-c^2}c^6 S_Q(c^2)R_Q(c^2)\,\mathrm{d}c \,.
\end{aligned} \tag{116}$$

The function $R_Q(c^2)$ in the last expression is defined due to the action of the operator L_Q on the function $S_Q(c^2)(c_ic_j - \frac{1}{3}\delta_{ij}c^2)$

$$\frac{P}{\mu_0^Q}R_Q(c^2)\left(c_ic_j - \frac{1}{3}\delta_{ij}c^2\right) = L_Q\left(S_Q(c^2)\left(c_ic_j - \frac{1}{3}\delta_{ij}c^2\right)\right) . \tag{117}$$

Finally, the parameter γ_Q in (112)–(116) reflects the temperature dependence of the VC

$$\gamma_Q = \frac{2}{3}\left(1 - \frac{T}{\mu_0^Q(T)}\left(\frac{\mathrm{d}\mu_0^Q(T)}{\mathrm{d}T}\right)\right) .$$

The set of ten equations (112)–(116) is alternative to the 10 moment Grad equations.

The observation already made is that for Maxwell molecules we have: $S^{\mathrm{M.M.}} \equiv 1$, and $\mu_0^{\mathrm{M.M.}} \propto T$; thus $\gamma^{\mathrm{M.M.}} = \beta^{\mathrm{M.M.}} = 0$, $r^{\mathrm{M.M.}} = \alpha^{\mathrm{M.M.}} = \frac{1}{2}$, and (112)–(116)

becomes the 10 moment Grad system under a simple change of variables $\lambda\zeta_{ij} = \sigma_{ij}$, where λ is the proportionality coefficient in the temperature dependence of $\mu_0^{\text{M.M.}}$.

These properties (the function S_Q is a constant, and the VC is proportional to T) are true only for Maxwell molecules. For all other interactions, the function S_Q is not identical to one, and the VC $\mu_0^Q(T)$ is not proportional to T. Thus, the shortened alternative description is not equivalent indeed to the Grad moment description. In particular, for hard spheres, the exact expression for the function $S^{\text{H.S.}}$ (111) reads

$$S^{\text{H.S.}} = \frac{5\sqrt{2}}{16}\int_0^1 \exp(-c^2t^2)(1-t^4)\big(c^2(1-t^2)+2\big)\,\mathrm{d}t, \quad \mu_0^{\text{H.S.}} \propto \sqrt{T}\,. \tag{118}$$

Thus, $\gamma^{\text{H.S.}} = \frac{1}{3}$, and $\frac{\beta^{\text{H.S.}}}{r^{\text{H.S.}}} \approx 0.07$, and the equation for the function ζ_{ik} (116) contains a nonlinear term

$$\theta^{\text{H.S.}}\zeta_{ik}\partial_s u_s\,, \tag{119}$$

where $\theta^{\text{H.S.}} \approx 0.19$. This term is missing in the Grad 10 moment equation.

Finally, let us evaluate the VC which results from the alternative description (112)–(116). Following Grad's arguments [19], we see that, if the relaxation of ζ_{ik} is fast compared to the hydrodynamic variables, then the two last terms in the equation for ζ_{ik} (112)–(116) become dominant, and the equation for $\boldsymbol{u}$ casts into the standard Navier–Stokes form with an effective VC μ_{eff}^Q

$$\mu_{\text{eff}}^Q = \frac{1}{2\alpha_Q}\mu_0^Q\,. \tag{120}$$

For Maxwell molecules, we easily derive that the coefficient α_Q in (120) is equal to $\frac{1}{2}$. Thus, as one expects, the effective VC (120) is equal to the Grad value, which, in turn, is equal to the exact value in the frames of the Chapman–Enskog method for this model.

For all interactions different from the Maxwell molecules, the VC μ_{eff}^Q (120) is not equal to μ_0^Q. For hard spheres, in particular, a computation of the VC (120) requires information about the function $R^{\text{H.S.}}$ (117). This is achieved upon a substitution of the function $S^{\text{H.S.}}$ (118) into (117). Further, we have to compute the action of the operator $L^{\text{H.S.}}$ on the function $S^{\text{H.S.}}(c_ic_j - \frac{1}{3}\delta_{ij}c^2)$, which is rather complicated. However, the VC $\mu_{\text{eff}}^{\text{H.S.}}$ can be relatively easily estimated by using a function $S_a^{\text{H.S.}} = \frac{1}{\sqrt{2}}(1+\frac{1}{7}c^2)$, instead of the function $S^{\text{H.S.}}$ in (117). Indeed, the function $S_a^{\text{H.S.}}$ is tangent to the function $S^{\text{H.S.}}$ at $c^2 = 0$, and is its majorant (see Fig. 3). Substituting $S_a^{\text{H.S.}}$ into (117), and computing the action of the collision integral, we find the approximation $R_a^{\text{H.S.}}$; thereafter we evaluate the integral $\alpha^{\text{H.S.}}$ (116), and finally come to the following expression:

$$\mu_{\text{eff}}^{\text{H.S.}} \geqslant \frac{75264}{67237}\mu_0^{\text{H.S.}} \approx 1.12\mu_0^{\text{H.S.}}\,. \tag{121}$$

Thus, for hard spheres, the description in terms of scattering rates results in the VC of more than 10% higher than in the Grad moment description.

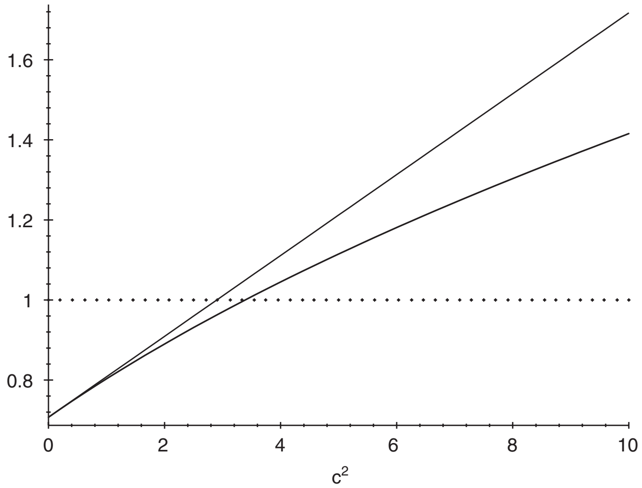

Fig. 3. Approximations for hard spheres: bold line—function $S^{\mathrm{H.S.}}$, solid line—approximation $S_a^{\mathrm{H.S.}}$, dotted line—Grad moment approximation.

A discussion of the results concerns the following two items.

1. Having two not equivalent descriptions which were obtained within one method, we may ask: which is more relevant? A simple test is to compare characteristic times of an approach to hydrodynamic regime. We have $\tau_G \sim \mu_0^{\mathrm{H.S.}}/P$ for 10-moment description, and $\tau_a \sim \mu_{\mathrm{eff}}^{\mathrm{H.S.}}/P$ for alternative description. As $\tau_a > \tau_G$, we see that scattering rate decay slower than corresponding moment, hence, at least for rigid spheres, the alternative description is more relevant. For Maxwell molecules both the descriptions are, of course, equivalent.

2. The VC $\mu_{\mathrm{eff}}^{\mathrm{H.S.}}$ (121) has the same temperature dependence as $\mu_0^{\mathrm{H.S.}}$, and also the same dependence on a scaling parameter (a diameter of the sphere). In the classical book [33] (pp. 228–229), "sizes" of molecules are presented, assuming that a molecule is represented with an equivalent sphere and VC is estimated as $\mu_0^{\mathrm{H.S.}}$. Since our estimation of VC differs only by a dimensionless factor from $\mu_0^{\mathrm{H.S.}}$, it is straightforward to conclude that effective sizes of molecules will be reduced by the factor b, where $b = \sqrt{\mu_0^{\mathrm{H.S.}}/\mu_{\mathrm{eff}}^{\mathrm{H.S.}}} \approx 0.94$. Further, it is well known that sizes of molecules estimated via viscosity in Ref. [33] disagree with the estimation via the virial expansion of the equation of state. In particular, in book [45, p. 5], the measured second virial coefficient B_{exp} was compared with the calculated B_0, in which the diameter of the sphere was taken from the viscosity data. The reduction of the diameter by factor b gives $B_{\mathrm{eff}} = b^3 B_0$. The values B_{exp} and B_0 [45] are compared with B_{eff} in the Table 1 for three gases at $T = 500\,\mathrm{K}$. The results for argon and helium are better for B_{eff}, while for nitrogen B_{eff} is worth than B_0. However, both B_0 and B_{eff} are far from the experimental values.

Table 1
Three virial coefficients: experimental B_{exp}, classical B_0 [45], and reduced B_{eff} for three gases at $T = 500\,\mathrm{K}$

	B_{exp}	B_0	B_{eff}
Argon	8.4	60.9	50.5
Helium	10.8	21.9	18.2
Nitrogen	168	66.5	55.2

Hard spheres is, of course, an oversimplified model of interaction, and the comparison presented does not allow for a decision between $\mu_0^{\mathrm{H.S.}}$ and $\mu_{\mathrm{eff}}^{\mathrm{H.S.}}$. However, this simple example illustrates to what extend the correction to the VC can affect a comparison with experiment. Indeed, as it is well known, the first-order Sonine polynomial computation for the Lennard–Jones (LJ) potential gives a very good fit of the temperature dependence of the VC for all noble gases [46], subject to a proper choice of the two unknown scaling parameters of the LJ potential.[2] We may expect that a dimensionless correction of the VC for the LJ potential might be of the same order as above for rigid spheres. However, the functional character of the temperature dependence will not be affected, and a fit will be obtained subject to a different choice of the molecular parameters of the LJ potential.

The five-parametric family of pair potentials was discussed in Ref. [47]. These five constants for each pair potential have been determined by a fit to experimental data with some additional input from theory. After that, the Chapman–Enskog formulas for the second virial coefficient and main transport coefficients give satisfactory description of experimental data [47]. Such a semi-phenomenological approach that combines fitting with kinetic theory might be very successful in experimental data description, but does not allow us to make a choice between hierarchies. We need to decide which hierarchy is better. This choice requires less flexibility in the potential construction. The best solution here is independent determination of the interaction potential without references to transport coefficients or thermodynamic data.

8. Conclusion and outlook

We developed the TEM for model reduction and demonstrated how it works for the Boltzmann equation. Moments of the Boltzmann collision integral, or scattering rates are treated as independent variables rather than as infinite moment series. Three classes of reduced models are constructed. The models of the first class involve only moments of distribution functions, and coincide with those of the Grad method in the Maximum Entropy version. The models of the second type involves only scattering rates. Finally, the mixed description models involve both the moments and the scattering rates. TEM allows us to obtain all the closure formulas in explicit form, not only for the Maxwell molecules (as it is usual), but for hard spheres also.

---

[2] A comparison of molecular parameters of the LJ potential, as derived from the viscosity data, to those obtained from independent sources, can be found elsewhere, e.g., in Ref. [33, p. 237].

We found the new Boltzmann-kinetics estimations for the equivalent hard sphere radius for gases.

The main benefits from TEM are:

(1) It constructs the closure as a solution of linear equations, and, therefore, often gives it in an explicit form;
(2) It provides the thermodynamic properties of reduced models, at least, locally;
(3) It admits nonlinear functionals as macroscopic variables, this possibility is important for creation of nonequilibrium thermodynamics of nonlinear fluxes, reaction rates, scattering rates, etc.

The following fields for future TEM applications are important:

- Modelling of nonequilibrium processes in gases (Boltzmann kinetics and its generalizations);
- Chemical kinetics models with reaction rates as independent variables;
- Kinetics of complex media (non-Newtonian liquids, polymers, etc.) with the Fokker–Planck equation as the basic kinetic description.

Renewed interest in MaxEnt methods is partly because of rapid development of nonextensive entropies [48,49]. In that sense, the Fokker–Plank equation seems to be an attractive example for MaxEnt method application [51], and, in particular, for the application of TEM. This classical equation admits a broad class of Lyapunov functions, including the classical Kulback form entropy [50,51] and nonextensive entropies [15].

For any hierarchy of equations the crucial question is: where to stop? Is it possible to decide, is a particular model from the hierarchy sufficiently accurate, or we need to go ahead? Without criteria for making such a decision we have just infinite number of theories.

The residual estimates are possible: we can estimate the defect of invariance (see Fig. 1). If it is too big (in comparison with the full right-hand side J), then we should switch to the next system of hierarchy. If it vanishes, we could try the previous system. Normally, it is impossible to find one reduced model for all regimes, but it is possible to change the model during simulation.

There exists one more benefit from the hierarchy. For each model we have an approximate slow invariant manifold Ω_i, and the vector field of the reduced dynamics J_i which is defined at points from Ω_i and is tangent to this manifold. This structure gives a possibility to estimate not the whole defect of invariance, but a "partial defect" $\Delta_i = J_{i+1} - J_i$. Usually it is sufficient to estimate this partial defect of invariance, that is, to check whether the current model is the approximate slow invariant manifold for the next model up to desired accuracy. Examples of these estimates and applications are presented in Refs. [15,16,29,38]. We propose to use the flexible technology of modelling with adaptive choice of the model from hierarchy. This approach could be discussed as intermediate one between the classical one-model calculations and the equation-free approach [52], for example.

We construct the quasiequilibrium hierarchy of models for a system with entropy growth. These systems relax to equilibrium points. But most interesting application is modelling of open systems. It is possible to use obtained hierarchy of models for open systems just by adding flows under the assumption that the fast motion and slow manifold do not change due to the system opening. For example, we usually use the Navier–Stokes equation for systems with external flows that do not relax to equilibrium. If the external flows are fast and the perturbation of slow manifold is significant, then the correspondent perturbation theory [15,16] modifies the model for open system.

The inertial manifold [13,53,54] is the manifold where the limit behaviour of the system is located; it exponentially attracts motions when $t \to \infty$. For a closed system the equilibrium (one point) is already the inertial manifold. In the theory of inertial manifolds the estimates of inertial manifolds dimension for several classes of (open) systems are created and finiteness of this dimension is proved. Inertial manifolds could be considered as the lowest level of any hierarchy of slow manifolds. They belong to all the slow invariant manifolds of the hierarchy. In our construction we build the hierarchy of infinite-dimensional approximate slow manifolds for the Boltzmann equation and do not try to find the smallest invariant manifolds for open systems.

And, finally, we should ask the question: what chain is better, could we prove that the second hierarchy with scattering rates instead of usual moments is better than the standard Grad hierarchy? We cannot prove this exactly, but can only argue plausibly that the second hierarchy should lead to dynamic invariance faster, than the first one, and support this point of view by examples.

Appendix A. Formulas of the second quasiequilibrium approximation for Maxwell molecules and hard spheres

Let us write v_{Qik} (71) in the standard form

$$v_{Qik} = \int f^{(0)} \mid \boldsymbol{v}_1 - \boldsymbol{v} \mid \left\{ (v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v} - \boldsymbol{u})^2 \right\} b \, \mathrm{d}b \, \mathrm{d}\varepsilon \, \mathrm{d}\boldsymbol{v}_1 \,, \tag{122}$$

where b is the impact parameter, ε is the angle between the plane containing the trajectory of the particle being scattered in the system of the centre of mass and the plane containing the entering asymptote, the trajectory, and a certain fixed direction. It is convenient to switch to the dimensionless velocity $\mathbf{c}$ and to the dimensionless relative velocity $\mathbf{g}$

$$c_i = \left(\frac{m}{2k_{\mathrm{B}}T}\right)^{1/2} (v_i - u_i), \quad g_i = \frac{1}{2}\left(\frac{m}{k_{\mathrm{B}}T}\right)^{1/2} (v_{1i} - u_i) \,. \tag{123}$$

After standard transformations and integration with respect to ε (see Ref. [33]) we obtain in (123)

$$\begin{aligned} v_{Qik} = {} & \frac{3P}{m}\pi^{-1/2} \\ & \times \int \exp(-c_1^2)\varphi_1^{(2)}(g)\left((c_{1i} - c_i)(c_{1k} - c_k) - \frac{1}{3}\delta_{ik}(\mathbf{c}_1 - \mathbf{c})^2\right) \mathrm{d}\mathbf{c}_1 \,. \end{aligned} \tag{124}$$

Here

$$\varphi_1^{(2)} = \int (1-\cos^2\chi) \mid \boldsymbol{v}_1 - \boldsymbol{v} \mid b(\chi) \left|\frac{\mathrm{d}b}{\mathrm{d}\chi}\right| \mathrm{d}\chi \tag{125}$$

and χ is an angle between the vectors g and g'.

The dependence of $\varphi_1^{(2)}$ on the vector g is determined by the choice of the model of particle's interaction.

For Maxwell molecules

$$\varphi_1^{(2)} = \left(\frac{2\kappa}{m}\right)^{1/2} A_2(5)\,, \tag{126}$$

where κ is a force constant, $A_2(5)$ is a number, $A_2(5) \approx 0.436$.

For the model of hard spheres

$$\varphi_1^{(2)} = \frac{\sqrt{2}\sigma^2}{3}\left(\frac{k_{\mathrm{B}}T}{m}\right)^{1/2} \mid \mathbf{c}_1 - \mathbf{c} \mid \,, \tag{127}$$

where σ is diameter of the sphere modelling the particle.

Substituting (126) and (127) into (125), we transform the latter to the form: for Maxwell molecules

$$\begin{aligned} v_{Qik} &= \frac{3P}{4m}\left(\frac{2\kappa}{\pi m}\right)^{1/2} A_2(5)\,\exp(-c^2)\left(\frac{\partial}{\partial c_i}\frac{\partial}{\partial c_k} - \frac{1}{3}\delta_{ik}\frac{\partial}{\partial c_s}\frac{\partial}{\partial c_s}\right)T^{\mathrm{M.M.}}(c^2)\,, \\ T^{\mathrm{M.M.}}(c^2) &= \int \exp(-x^2 - 2x_k c_k)\,\mathrm{d}\boldsymbol{x} \end{aligned} \tag{128}$$

for hard spheres

$$\begin{aligned} v_{Qik} &= \frac{P\sigma^2}{2\sqrt{2}m}\left(\frac{k_{\mathrm{B}}T}{\pi m}\right)^{1/2} \exp(-c^2)\left(\frac{\partial}{\partial c_i}\frac{\partial}{\partial c_k} - \frac{1}{3}\delta_{ik}\frac{\partial}{\partial c_s}\frac{\partial}{\partial c_s}\right)T^{\mathrm{H.S.}}(c^2)\,, \\ T^{\mathrm{H.S.}}(c^2) &= \int \mid \boldsymbol{x} \mid \exp(-x^2 - 2x_k c_k)\,\mathrm{d}\boldsymbol{x}\,. \end{aligned} \tag{129}$$

It is an easy matter to perform integration in (128), the integral is equal to $\pi^{3/2}e^{c^2}$.

Therefore for Maxwell molecules

$$v_{Qik} = \frac{3}{2}n\pi\left(\frac{2\kappa}{m}\right)^{1/2} A_2(5)\left((v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v} - \boldsymbol{u})^2\right)\,. \tag{130}$$

The integral $T^{\mathrm{H.S.}}$ in (129) can be transformed as follows:

$$T^{\mathrm{H.S.}}(c^2) = 2\pi + \pi\int_{-1}^{+1} \exp(c^2(1-y^2))c^2(1+y^2)\,\mathrm{d}y\,. \tag{131}$$

Then for the model of hard spheres

$$\nu_{Qik} = \sqrt{2\pi} n\sigma^2 \left(\frac{k_B T}{m}\right)^{3/2} \left(c_i c_k - \frac{1}{3}\delta_{ik} c^2\right) \times \int_{-1}^{+1} \exp(-c^2 y^2)(1+y^2)(1-y^2)(c^2(1-y^2)+2)\,\mathrm{d}y\,. \tag{132}$$

Let us note a useful relationship:

$$d^n T^{\mathrm{H.S.}}/d(c^2)^n = \pi \int_{-1}^{+1} \exp(c^2(1-y^2)) \times (1+y^2)(1-y^2)^{n-1}(c^2(1-y^2)+n)\,\mathrm{d}y, \quad n \geqslant 1\,. \tag{133}$$

Use the expressions for the viscosity coefficient μ_0 which are obtained in the first approximation of the Chapman–Enskog method: for Maxwell molecules

$$\mu_0^{\mathrm{M.M.}} = \left(\frac{2m}{\kappa}\right)^{1/2} \frac{k_B T}{3\pi A_2(5)} \tag{134}$$

for hard spheres

$$\mu_0^{\mathrm{H.S.}} = \frac{5(k_B T m)^{1/2}}{16\pi^{1/2}\sigma^2}\,. \tag{135}$$

Transformation of (130), (132) to the form of (74) gives the following functions $\Phi((\boldsymbol{v}-\boldsymbol{u})^2)$: for Maxwell molecules

$$\Phi = P/\mu_0^{\mathrm{M.M.}} \tag{136}$$

for hard spheres

$$\Phi = \frac{5P}{16\sqrt{2}\mu_0^{\mathrm{H.S.}}} \int_{-1}^{+1} \exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_B T} y^2\right) \times (1+y^2)(1-y^2)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_B T}(1-y^2)+2\right)\mathrm{d}y\,. \tag{137}$$

The parameter r from (75) is for Maxwell molecules

$$r = (m\mu_0^{\mathrm{M.M.}})^2/(2P^3 k_B T) \tag{138}$$

for hard spheres

$$r = \tilde{r}\frac{64(m\mu_0^{\mathrm{M.M.}})^2}{25P^3 k_B T}\,. \tag{139}$$

The dimensionless parameter $\tilde{r}$ is represented as follows:

$$\tilde{r}^{-1} = \frac{1}{16}\int_{-1}^{+1}\int_{-1}^{+1} \alpha^{-11/2}\beta(y)\beta(z)\gamma(y)\gamma(z) \times (16\alpha^2 + 28\alpha(\gamma(y)+\gamma(z)) + 63\gamma(y)\gamma(z))\,\mathrm{d}y\,\mathrm{d}z\,. \tag{140}$$

Here and below the following notations are used:

$$\beta(y) = 1 + y^2, \quad \gamma(y) = 1 - y^2, \quad \alpha = 1 + y^2 + z^2\,. \tag{141}$$

Numerical value of $\tilde{r}^{-1}$ is 5.212 to third decimal point.

The parameter (83) is for Maxwell molecules

$$s^{-1} = (2P^2 k_{\mathrm{B}} T)/(m^2 \mu_0^{\mathrm{M.M.}}) \tag{142}$$

for hard spheres

$$s^{-1} = \tilde{s}^{-1} \frac{5\sqrt{2} P^2 k_{\mathrm{B}} T}{8 m^2 \mu_0^{\mathrm{H.S.}}}\,. \tag{143}$$

The dimensionless parameter $\tilde{s}^{-1}$ is of the form

$$\tilde{s}^{-1} = \int_{-1}^{+1} \gamma(y) \beta^{-7/2}(y) \left(\beta(y) + \frac{7}{4} \gamma(y) \right) \mathrm{d}y\,. \tag{144}$$

Numerical value of $\tilde{s}^{-1}$ is 1.115 to third decimal point.

The scattering rate density (90) is of the form

$$\xi_{Qi} = \sqrt{2} \left(\frac{k_{\mathrm{B}} T}{m} \right)^{3/2} \int f^{(0)}(\boldsymbol{v}_1) \mid \boldsymbol{v}_1 - \boldsymbol{v} \mid \left\{ c_i \left(c^2 - \frac{5}{2} \right) \right\} b \, \mathrm{d}b \, \mathrm{d}\varepsilon \, \mathrm{d}\boldsymbol{v}_1\,. \tag{145}$$

Standard transformation of the expression $\{c_i(c^2 - 5/2)\}$ and integration with respect to ε change (145) to the form

$$\xi_{Qi} = \frac{P}{\sqrt{2\pi} m} \int \exp(-c_1^2) \varphi_1^{(2)} (3(c_1^2 - c^2)(c_{1i} - c_i) - (\mathbf{c}_1 - \mathbf{c})^2 (c_{1i} + c_i)) \, \mathrm{d}\mathbf{c}_1\,. \tag{146}$$

Further, using the expressions (126) and (127) for $\varphi_1^{(2)}$, we obtain for Maxwell molecules

$$\xi_{Qi} = \frac{P}{m^2} \left(\frac{\kappa k_{\mathrm{B}} T}{\pi} \right)^{1/2} A_2(5) \exp\left(-c^2\right) \hat{D}_i T^{\mathrm{M.M.}}(c^2) \tag{147}$$

for hard spheres

$$\xi_{Qi} = \frac{P k_{\mathrm{B}} T \sigma^2}{\sqrt{\pi} m^2} \exp(-c^2) \hat{D}_i T^{\mathrm{H.S.}}(c^2)\,. \tag{148}$$

The operator $\hat{D}_i$ is of the form

$$\frac{1}{4} \frac{\partial}{\partial c_i} \frac{\partial}{\partial c_s} \frac{\partial}{\partial c_s} + \frac{3}{2} c_s \frac{\partial}{\partial c_s} \frac{\partial}{\partial c_i} - \frac{1}{2} c_i \frac{\partial}{\partial c_s} \frac{\partial}{\partial c_s}\,. \tag{149}$$

The operator $\hat{D}_i$ acts on the function $\psi(c^2)$ as follows:

$$\frac{\mathrm{d}^2 \psi}{\mathrm{d}(c^2)^2} 2 c_i \left(c^2 - \frac{5}{2} \right) + c_i c^2 \left(\frac{\mathrm{d}^2 \psi}{\mathrm{d}(c^2)^2} - \frac{\mathrm{d}^3 \psi}{\mathrm{d}(c^2)^3} \right)\,. \tag{150}$$

From (147) and (148) we obtain for Maxwell molecules

$$\xi_{Qi}=\frac{P}{3\mu_0^{\mathrm{M.M.}}}(v_i-u_i)\left((\boldsymbol{v}-\boldsymbol{u})^2-\frac{5k_{\mathrm{B}}T}{m}\right) \tag{151}$$

for hard spheres

$$\begin{aligned}\xi_{Qi}=\frac{5P}{16\sqrt{2}\mu_0^{\mathrm{H.S.}}}&\left\{(v_i-u_i)\left((\boldsymbol{v}-\boldsymbol{u})^2-\frac{5k_{\mathrm{B}}T}{m}\right)\right.\\&\times\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\beta(y)\gamma(y)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\gamma(y)+2\right)\mathrm{d}y\\&+(v_i-u_i)(\boldsymbol{v}-\boldsymbol{u})^2\\&\left.\times\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\beta(y)\gamma(y)\left(\sigma(y)\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}+\delta(y)\right)\mathrm{d}y\right\}.\end{aligned} \tag{152}$$

The functions $\sigma(y),\delta(y)$ are of the form

$$\sigma(y)=y^2(1-y^2),\quad \delta(y)=3y^2-1\,. \tag{153}$$

The parameter η from (95) is for Maxwell molecules

$$\eta=\frac{9m^3(\mu_0^{\mathrm{M.M.}})^2}{10P^3(k_{\mathrm{B}}T)^2} \tag{154}$$

for hard spheres

$$\eta=\tilde{\eta}\frac{64m^3(\mu_0^{\mathrm{H.S.}})^2}{125P^3(k_{\mathrm{B}}T)^2}\,. \tag{155}$$

The dimensionless parameter $\tilde{\eta}$ is of the form

$$\begin{aligned}\tilde{\eta}^{-1}=\int_{-1}^{+1}\int_{-1}^{+1}&\beta(y)\beta(z)\gamma(y)\gamma(z)\alpha^{-13/2}\left\{\frac{639}{32}(\gamma(y)\gamma(z)+\sigma(y)\sigma(z)\right.\\&+\sigma(y)\gamma(z)+\sigma(z)\gamma(y))+\frac{63}{16}\alpha(2\gamma(y)+2\gamma(z)-5\gamma(y)\gamma(z)\\&+2(\sigma(y)+\sigma(z))+\gamma(z)\delta(y)+\gamma(y)\delta(z)+\sigma(y)\delta(z)+\sigma(z)\delta(y))\\&+\frac{7}{8}\alpha^2(4-10\gamma(y)-10\gamma(z))+\frac{25}{4}\gamma(y)\gamma(z)+2\delta(y)\\&+2\delta(z)-5\sigma(y)-5\sigma(z)-\frac{5}{2}(\gamma(z)\delta(y)+\gamma(y)\delta(z)+\delta(y)\delta(z))\\&\left.+\frac{1}{4}\alpha^3\left(-20+\frac{25}{4}(\gamma(y)+\gamma(z))-5(\delta(y)+\delta(z))\right)+\frac{5}{2}\alpha^4\right\}\mathrm{d}y\,\mathrm{d}z\,.\end{aligned} \tag{156}$$

Numerical value of $\tilde{\eta}^{-1}$ is 0.622 to second decimal point.

Finally, from (151) and (153) we obtain τ^{-1} (102) for Maxwell molecules

$$\tau^{-1}=\frac{5(Pk_{\mathrm{B}}T)^2}{3\mu_0^{\mathrm{M.M.}}m^3} \tag{157}$$

for hard spheres

$$
\begin{aligned}
\tau^{-1} &= \tilde{\tau}^{-1}\frac{25P^2(k_{\mathrm{B}}T)^2}{8\sqrt{2}m^3\mu_0^{\mathrm{H.S.}}},\\
\tilde{\tau}^{-1} &= \frac{1}{8}\int_{-1}^{+1}\beta^{-9/2}(y)y\gamma(y)\{63(\gamma(y)+\sigma(y))\\
&\quad + 7\beta(y)(4-10\gamma(y)+2\delta(y)-5\sigma(y)) + 20\beta^3(y)\\
&\quad + \beta^2(y)(25\gamma(y)-10\delta(y)-40)\}\,\mathrm{d}y \approx 4.322\,. \qquad (158)
\end{aligned}
$$

Appendix B. Mixed chain

The closure of the mixed hydrodynamic chain with the functions (89) gives the following system of equations:

$$
\begin{aligned}
&\partial_t\rho + \partial_i(u_i\rho) = 0, \quad \rho(\partial_t u_k + u_i\partial_i u_k) + \partial_k P + \partial_i\sigma_{ik} = 0,\\
&\frac{3}{2}(\partial_t P + u_i\partial_i P) + \frac{5}{2}P\partial_i u_i + \sigma_{ik}\partial_i u_k = 0\,,
\end{aligned}
$$

$$
\begin{aligned}
&\partial_t\sigma_{ik} + \partial_s(u_s\sigma_{ik}) + P\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right)\\
&\quad + \sigma_{is}\partial_s u_k + \sigma_{ks}\partial_s u_i - \frac{2}{3}\delta_{ik}\sigma_{ls}\partial_s u_l + \Delta_{ik} = 0,
\end{aligned}
$$

$$
\begin{aligned}
&\partial_t\Delta_{ik} + \partial_s(u_s\Delta_{ik}) + \frac{5P^2}{\tilde{s}8\sqrt{2}\mu_0^{\mathrm{H.S.}}}\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right)\\
&\quad + \frac{5P}{4\sqrt{2}\mu_0^{\mathrm{H.S.}}(\tilde{s}^{-2}-\tilde{r}^{-1})}\left\{\frac{\tilde{a}_1}{2}(\partial_s u_s)\alpha_{ik}\right.\\
&\quad + \frac{1}{2}(\tilde{a}_1+\tilde{a}_2)\left(\alpha_{is}\partial_s u_k + \alpha_{ks}\partial_s u_i - \frac{2}{3}\delta_{ik}\alpha_{ls}\partial_s u_l\right)\\
&\quad + \frac{1}{2}(\tilde{a}_1+\tilde{a}_3)\left(\alpha_{is}\partial_k u_s + \alpha_{ks}\partial_i u_s - \frac{2}{3}\delta_{ik}\alpha_{ls}\partial_s u_l\right)\\
&\quad + \tilde{b}_1(\partial_s u_s)\beta_{ik} + (\tilde{b}_1+\tilde{b}_2)\left(\beta_{is}\partial_s u_k + \beta_{ks}\partial_s u_i - \frac{2}{3}\delta_{ik}\beta_{ls}\partial_s u_l\right)\\
&\quad \left. + (\tilde{b}_1+\tilde{b}_3)\left(\beta_{is}\partial_k u_s + \beta_{ks}\partial_i u_s - \frac{2}{3}\delta_{ik}\beta_{ls}\partial_s u_l\right)\right\}\\
&\quad + \frac{5P^2}{8\sqrt{2}(\mu_0^{\mathrm{H.S.}})^2(\tilde{s}^{-2}-\tilde{r}^{-1})}\left\{\frac{5}{8\sqrt{2}\tilde{r}}\beta_{ik} + \tilde{a}_0\alpha_{ik}\right\} = 0\,, \qquad (159)
\end{aligned}
$$

$$
\alpha_{ik} = \tilde{s}^{-1}\sigma_{ik} - \frac{8\sqrt{2}}{5P}\cdot\mu_0^{\mathrm{H.S.}}\Delta_{ik}, \quad \beta_{ik} = \tilde{s}^{-1}\frac{8\sqrt{2}}{5P}\cdot\mu_0^{\mathrm{H.S.}}\Delta_{ik} - \tilde{r}^{-1}\sigma_{ik}\,. \qquad (160)
$$

It is clear from the analysis of distribution functions of the second quasiequilibrium approximations of the second hydrodynamic chain that in the Grad moment method the function $\Phi(c^2)$ is substituted by a constant. Finally, let us note the simplest consequence of the variability of function $\Phi(c^2)$. If μ_0 is multiplied with a small parameter (Knudsen number Kn equal to the ratio of the main free path to the characteristic spatial scale of variations of hydrodynamic values), then the first with respect to Kn approximation of collision stress tensor $\Delta_{ik}^{(0)}$ has the form

$$\Delta_{ik}^{(0)} = P\left(\partial_i u_k + \partial_k u_i - \tfrac{2}{3}\delta_{ik}\partial_s u\right) \tag{161}$$

for Maxwell molecules, and

$$\Delta_{ik}^{(0)} = \frac{5\tilde{r}}{8\sqrt{2}\tilde{s}\tilde{a}_0} P\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right) \tag{162}$$

for hard spheres. Substitution of these expressions into the momentum equations results in the Navier–Stokes equations with effective viscosity coefficients μ_{eff}

$$\mu_{\text{eff}} = \mu_0^{\text{M.M.}} \tag{163}$$

for Maxwell molecules and

$$\mu_{\text{eff}} = \tilde{a}_0^{-1}\, \mu_0^{\text{H.S.}} \tag{164}$$

for hard spheres. When using ten-moment Grad approximation which does not distinguish Maxwell molecules and hard spheres, we obtain $\mu_{\text{eff}} = \mu_0^{\text{H.S.}}$.

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